Thermally reversible thermoset materials based on the chemical modification of alternating aliphatic polyketones

PhD thesis

to obtain the degree of PhD at the University of Groningen on the authority of the Rector Magnificus Prof. E. Sterken and in accordance with the decision by the College of Deans.

This thesis will be defended in public on

Monday 17 October 2016 at 16.15 hours

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Dedicado a mi amada familia

Dedicated to my beloved family
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1 Introduction

1.1 Thermosetting polymers

Thermosetting polymers constitute an important class of materials used for coatings, adhesives, and electrical insulators, among several other applications [1]. Thermosets, unlike thermoplastics, are characterized by a curing reaction that transforms two or more (liquid or paste [2]) components into a solid network structure. Due to this network, thermosets offer many superior properties compared to thermoplastics such as mechanical strength, dimensional stability at elevated temperature and solvent resistance. Overall, those features can be simply tuned by adjusting the crosslink density of the thermoset network, which in turn results in a wide range of applications [3]. In this chapter, the history of polyketones, their chemical modification routes and potential use as a thermosets will be briefly discussed and framed in the general context of thermosetting polymers.

Since the development of synthetic polymers like Bakelite (phenol-formaldehydes in 1909) many efforts have been spent at improving plastic features (e.g. strength, toughness, recyclability, etc). During the early twenties, all efforts were essentially based on a “trial and error” approach without any real definition of the “macromolecule” concept. It was at the end of the twenties that this concept appeared with the work of Hermann Staudinger (1920), who suggested the existence of macromolecules. After the twenties, polymers like PE (polyethylene in 1940) started to replace natural materials due to several advantages of synthetic polymers in several conventional applications (e.g. light weight, low cost, easiness of processing). These advantages quickly widespread the use of synthetic polymers in technological applications likes fabrics, coatings, structural materials, etc. It is during this period (1941) that Farbenfabriken Bayer synthesized polyketone (PK) by using free-radical polymerization (FRP) of ethylene and carbon monoxide [4]. In this first attempt, PK was synthesized under extreme conditions (400 bar and 250 °C) and characterized as a random distributed polymer (non-alternating). During the next 10 years, more research efforts were spent in order to optimize the polymerization process. Indeed, Badische Anilin und Soda-Fabrik Aktiengesellschaft (1951) synthesized a perfect alternating PK using K₂Ni(CN)₄ as catalyst (Figure 1.1) [5]. Thirty years later, researcher from Shell improved the polymerization process of PK using a bidentate-Pd²⁺ phosphine catalyst. Remarkably, the use
of this catalyst enlarged the polymerization rate of PK (6 kg PK/g Pd\(^{-1}\) hr\(^{-1}\)) under mild conditions of temperature and pressure (50-60 bar and 70-135 °C) [6].

![Chemical reaction](Image)

**Figure 1.1** Alternating ethylene carbon monoxide polyketone [7].

During the nineties, several research articles have been published dealing, among others, with a wide spreading range of potential application for PK. This stemmed from the industrial scale by which PK can be produced and mainly consisted in the mixing with organic additives and curing at high temperature [8, 9]. Nowadays, the chemical modification of PK with amine compounds (the so-called Paal-Knorr reaction) has been gaining a lot of attention. This is related to the tolerance of this reaction towards many functional groups, particularly sterically hindered amine groups [10] (Figure 1.2).

![Chemical modification](Image)

**Figure 1.2** Schematic representation of the chemical modification of polyketone via Paal-Knorr reaction with amine compounds.

This synthetic pathway offers several advantages like high yield under relatively mild condition (100 °C) and reaction kinetics (4 h) even without any catalyst, with water as the only by-product. Notably, the easy chemical modification and low production costs allowed the preparation of polymeric surfactants and nano-emulsions used for wood adhesives application [11]. In 2009, Zhang and his co-workers published the first attempt for the
chemical modification of PK with furan amino-substituted compounds aiming at preparing thermoset polymer networks able to undergo reversible reactions via Diels-Alder (DA) chemistry. The furan groups grafted directly on the PK backbone chain allowed the formation of a three-dimensional network structure after being cross-linked with aromatic bis-maleimide. The material indeed formed a thermally reversible and self-healing thermoset polymer by means of DA and retro-DA sequence [12]. The properties of the resulting product could be easily tuned by changing the crosslink density.

The cross-linking density in thermoset systems allows tailoring many aspects on their thermo-mechanical properties. However, as the cross-linking density is increased, some positive and negative effects can appear. For instance, highly cross-linked systems typically display good mechanical properties such as hardness and modulus, and also remarkable solvent resistance. Contrarily, highly cross-linked densities also give poor elongation, low impact strength and toughness. Usually, a low cross-linked polymer system behaves as a flexible material whereas a highly cross-linked one behaves as a brittle system. A trade-off between high and low cross-linking density values is then necessary in order to achieve the required properties for any given application. An example of DMTA thermograms for PK-furan containing thermosets with different crosslink densities is displayed in Figure 1.3.

![DMTA thermograms for PK50 functionalized with furan groups](image)

**Figure 1.3** Loss (Δ) and storage (□) modulus behavior in DMTA cycles for PK50 functionalized with furan groups (A) at different crosslink densities: (a) 1:1, (b) 1:0.5 and (c) 1:0.25 molar ratios between furan and bis-maleimide. The softening point, taken as tan (δ) of the respective samples, is displayed in (B) [13].
It is clear that at higher furan/bis-maleimide molar ratios (i.e. at lower cross-linking density values), the softening point is also diminished, thus indicating a less stiff material.

1.2 Reversible thermoset polymers

Polymer materials are nowadays essential in our society. In almost any single application, polymers have found spots as structural or multifunctional materials. As the demand is growing, the depleting of natural sources (e.g. petroleum) makes urgent the creation of effective solutions on these concerns. Overcoming this huge disequilibrium between the production of synthetic polymers and the depletion of natural resources, recyclable materials have emerged as suitable solutions. Typically, polymers degrade with the use and age due to mechanical stress. For instance, in an early stage of damage, unnoticed micro-cracks appear which can lead to macro levels of damage and the failure of the whole system. The re-join of cracks in conventional polymer systems can be achieved in different ways, like patching with the same material or adhesives. However, the original mechanical properties of the system will never be completely recovered. This is particularly true for thermosets, where the chemical bonds between the chains can factually not be broken (which would allow re-processing of the material) without any detrimental effect on the C-C bonds along the backbone [14]. On the contrary, reversible polymeric networks can be continuously repaired just using external stimulus like heat, pressure and light. In any case, the reversible process of polymerization, branching or cross-linking allows in principle the recovery of the original mechanical properties. Such reversible properties usually depend on the cleavage and reconnection of covalent bonds. However non-covalent supramolecular interactions like π-π staking and hydrogen bonding are also able to perform the reconnection of a severed join under the influence of an external stimulus [15].

Reversible thermoset polymers represent a breakthrough in the general field of renewable materials. For instance, upon thermal stimulus, thermally reversible thermosets are able to disconnect joint functional groups and reconnect them after cooling. This is a great advantage since polymers or even monomers can be recovered after the end of service life of a certain material. Besides, when a reversible system undergoes a catastrophic failure, the re-join of functional groups can recover the damaged region, thus factually extending in time the function and service life of the material.
The concept of a reversible network is the conceptual basis of reworkability as well as self-healing polymers, which will be discussed in the next section.

### 1.3 Self-healing polymer systems

Repair strategies for self-healing systems are commonly relying on active repairing approaches. As a damage event occurs, external repairing agents (extrinsic approach) embedded in a polymer matrix or the inherent functionality of certain moieties from the polymer (intrinsic approach) will be activated in order to begin the process of repairing. This can take place either using the damage as a trigger or using an external stimulus for healing (Figure 1.4). Intrinsic systems, avoiding the use of any additive, would be in principle preferable over extrinsic ones. However, the engineering and device of an intrinsic autonomous system is still a biological attribute difficult to homologate in synthetic systems.

![Figure 1.4 Extrinsic and intrinsic self-healing chemistry of polymer networks [16].](image)

Intrinsic self-healing systems, as mentioned above, rely on special attributes of functional groups and the nature of the polymer matrix. In general, these kinds of systems are able to repair cracks upon external stimulus. Autonomous intrinsic self-repairing systems are so far a difficult task for material engineering and just few examples have been mentioned which mostly relay on reversible hydrogen bonding interactions [17-20]. As it was addressed, intrinsic self-healing systems are based on molecular mechanisms for the repairing process.
The next paragraphs will briefly define the mechanisms involved in physical, chemical and supramolecular interactions currently used for intrinsic self-healing systems.

**Physical self-healing**

One of the most common procedures for reversible physical interactions is through thermal activation of the polymer chains. This was firstly studied by Wool and O’Connor for thermoplastic materials [21]. In that work, they pointed out that crack healing proceeds through five different stages. During thermal activation, a crack edge will start to undergo: a) surface rearrangement that depends on the nature of the polymer material, b) the approach of crack edges that will depend on the molecular density of polymer chains in the damage region, c) wetting, d) diffusion that controls the recovery of mechanical properties and e) randomization of the last conformation and entanglement of polymer chains (Figure 1.5). In a real case, crack healing is carried out by heating the sample above its $T_g$ to ensure reptation of the molecules. If the reptation of the polymer chains is not achieved, a low pressure is used to connect crack edges. After this, the mechanical strength is recovered thanks to the inter-diffusion and re-entanglement of polymer chains. As a result of this procedure of welding (which relies on the same steps but using higher activation energies), the mechanical strength and toughness of cracked edges are usually recovered. The recovery degree (i.e. the degree at which the properties can be recovered with respect to the original ones) crucially depends on the period of the heat treatment. Prolonged exposure to healing stimuli (such as heat) could actually result in relatively low recovery degree due to obvious side effects. Therefore, the functionalization of polymers with active functional groups (e.g. reversible covalent or hydrogen bonding interactions) able to recover damage in a short period of time and with low energy could play a crucial role in order to decrease the time of exposure of the material to healing/damaging conditions (e.g. high temperature).

As previously discussed, self-healing mechanisms are meant to re-crosslink damaged regions on polymer networks either by physical or chemical interactions. The latter relies on certain functional groups pending from the polymer chains and able to perform the re-connection of polymer networks after been severed.
Chemical self-healing

In the case of reversible covalent bonds, a reversible mechanism is involved in order to achieve the reconnection and diffusion of polymer chains at damage interfaces. However, the process of reconnection of covalent chemical bonds usually requires relatively high levels of energy in order to ensure the complete recovery of damage. Contrarily, supramolecular self-healing is based on the link of supramolecular interactions that experience high mobility at low levels of energy that ensures the faster recovery of a damaged region. In the next two sections, both concepts commonly classified as “reversible covalent and supramolecular networks” will be addressed in order to clarify the chemistry involved behind both concepts.

Reversible covalent network formation

One of the most emblematic examples of reversible covalent bonding is the Diels-Alder (DA) cycloaddition reaction [23]. The reaction take place between C-C bonds and is typically in high yield due to a good stereochemistry. Commonly, electrochemically activated diene (4π) and dienophile (2π) compounds react to form a cycloadduct (4+2) (Figure 1.6).
Two stereochemically different products are mostly formed: the so-called endo and exo DA adducts. The endo conformation is the kinetic product, the exo conformation is the thermodynamically favourable product thanks to the less steric hindrance. As a special feature, this kind of reaction is reversible upon heating (cycloreversion), which is commonly known as retro-Diels-Alder reaction (r-DA) (Figure 1.7).

This reaction is been widely used in self-healing polymeric systems due to several reasons: the weaker bond between diene and dienophile compounds, compared to conventional covalent bonds, will be primarily broken during a damage event. However, upon heating the crack will be recovered due to segmental mobility and reconnection of the DA active groups. Among all possible alternatives, the Diels-Alder cycloaddition between furan and maleimide moieties is indeed one of the most exploited in thermoreversible cross-linking for several reasons. First, DA is an equilibrium reaction influenced by temperature: covalent furan/maleimide adducts are formed at about 50 °C (cross-linking) and broken (de-cross-
linking via r-DA) at about 120 °C. Furthermore, the cross-linking and de-cross-linking process can be repeated many times with negligible degradation in the range of 50 °C – 150 °C. Finally, the strong dienic character of the furan ring and the high reactivity of the maleimide as a dienophile, ensure fast kinetics and high yields. According to literature reviews, most of the studied thermo-reversible networks are based on DA reaction of polymers bearing pendant furan and/or maleimide groups [15, 25-29]. For instance, a system based on alternating aliphatic polyketones with pending furan groups and cross-linked with 1,1’-(methylenedi-4,1-phenylene)bis-maleimide was proposed as a promising low cost and efficient thermally reversible system (Figure 1.8). As mentioned above, alternating aliphatic polyketones obtained by copolymerization of carbon monoxide, ethylene and propylene were modified through the Paal-Knorr reaction in order to introduce furan groups directly attached to the PK backbone chain. The thermoset obtained upon cross-linking with bis-maleimide was indeed re-healed up to seven times and displayed quantitatively retained mechanical properties [12].

Figure 1.8 Thermally reversible and self-healing polyketone thermoset [12].

Supramolecular network formation

Self-healing polymer networks based on supramolecular bonds have been extensively studied [15]. One of the main advantages obtained from reversible supramolecular bonds is the timescale for damage recovery. Hence, reversibility, directionality and sensitivity make
supramolecular interactions excellent candidates in the creation of self-healing materials. However, the resulting network formation of supramolecular bonds is rather weaker than reversible covalent bonds. For instance, self-healing polymers based on supramolecular interactions like hydrogen bonding or π-π stacking have the ability to recover severed bonds thanks to the sticker-like behaviour of these interactions that enable the connection and reconnection of broken networks upon heating [30]. However, they usually exhibit low Tg and relatively soft mechanical properties, which hinder their potential application as structural materials. In particular, polymer networks based on hydrogen bonding can form clusters of hydrogen moieties depending on the acidity of the hydrogen donors. It is worth mentioning that this represents a great advantage considering that the reversible properties can be tuned according to the amount and modes of interaction of the hydrogen donors with its hydrogen acceptor. In short, the kind of interaction will determine how strong the material is and how fast and effective the healing process will be. An excellent control of highly directional interactions between hydrogen donors and acceptors can result in a strong reversible cross-linked polymer network as is displayed in Figure 1.9.

![Figure 1.9](image)

**Figure 1.9** Schematic representation of reversible multiple hydrogen bonding interactions between 2-ureido-4-pyrimidone molecules [31].

In this example, a very well organized molecular architecture is achieved via quadruple hydrogen bonds using (2-ureido-4-pyrimidones) building blocks which indeed display multiple hydrogen bonding. The reversible thermal activation of the polymeric material was found at 90 °C, when the viscosity substantially decreases, allowing the reconnection of the hydrogen bonds. Moreover, the material indeed found application in the real world as a reversible elastomer and was adopted by the industry as a commercial product known as SupraPolix [20].
Self-healing polymers based on π-π stacking interactions represent a convenient approach in reversible systems using a thermal trigger to obtain healing processes. In particular, these kinds of systems take advantage by combining π-electron rich and π-electron poor functional groups as can be observed in Figure 1.10.

![Figure 1.10 Schematic representation of reversible π-π stacking interactions between copolyimide and pyrenyl end-capped chains [30].](image)

In this example, a self-healing material based on π-π stacking interactions was achieved by the combination of a short polymeric chain containing pyrenyl end-groups (π-electron deficient), which interact with a long molecular chain containing π-electron-rich imide aromatic groups. The $T_g$ of the network was tuned in order to achieve the healing process in a range of temperature between 50 and 100 °C by adjusting the ratio between the components. By increasing the temperature of the system, the disruption of the π-π stacking interactions between functional groups is promoted. This allows the flow and re-entanglement of the polymer chains at the damaged region. After cooling, the reformation of the π-π stacking re-establishes the network and the mechanical strength of the material [32].

1.4 Aim of the thesis

This thesis is focused on the synthesis and characterization of different kinds of reversible thermosets and thermoset nanocomposite materials by using alternating aliphatic polyketone (PK) as raw material. Through the different chapters, fundamental knowledge is obtained regarding the molecular design of polymers via chemical modification of PK with aliphatic and aromatic amine compounds. The resulting thermally reversible systems are investigated to outline the benefits for the synergistic cooperation between reversible covalent and supramolecular interactions. Moreover, improvements regarding the mechanical
performance, reversibility, recyclability, self-healing and electrical conductivity of the thermoset systems have been investigated including the addition of rubber particles and nanofillers to generate suitable industrial materials.

Chapters 2 and 3 focus on the chemical modification of alternating aliphatic polyketone with aliphatic and aromatic amine compounds using the Paal-Knorr reaction to obtain thermally reversible polymers with relatively high glass transition temperatures (i.e. a $T_g$ window from 100 to 185 °C). Both chapters highlight the tunable thermal properties of polymers containing furan (Diels-Alder) and hydrogen bonding active groups directly attached to the backbone. The reversible thermosetting of furan-functionalized polymers via a Diels-Alder and retro-Diels-Alder sequence with bis-maleimide is investigated and systematically compared with thermoset polymers containing both reversible covalent and supramolecular interactions.

Chapter 4 reports on the preparation of a reversible and toughened thermoset system based on the covalent incorporation of furan-functionalized ethylene-propylene rubber into a thermoset furan-functionalized polyketone. Analytical, thermo-mechanical and morphological studies have been carried out to evaluate the impact strength, reworkability and recyclability of the toughened thermoset material.

Chapter 5 focuses on the design of an engineered thermoplastic polymer containing pyrrole units in the main chain and hydroxyl pendant groups, which help in achieving nanocomposites containing well-distributed, exfoliated and undamaged MWCNTs. The incorporation of MWCNTs made it possible to change the material from an insulator to a conductive system displaying temperature sensor properties. Notably, the resistivity–temperature profile is very reproducible which suggests the potential application of the composite as a temperature sensor.

Chapter 6 describes the electrically-induced self-healing properties of a thermoset nanocomposite designed by mixing furan-functionalized polyketone cross-linked with aromatic bis-maleimide and MWCNTs via Diels-Alder (DA) reversible cycloaddition. The incorporation of MWCNTs increases the material modulus and allowed electrical conduction. It is also demonstrated that above the thermal stability of the composite, the retro-DA process is triggered reducing the mechanical properties of the material due to the decoupling of DA adducts. Nevertheless, the mechanical properties are completely recovered after the sample is healed through electrical resistive heating.
## 1.5 References

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2 Reversible polymer networks containing covalent and hydrogen bonding interactions

Abstract. Thermally reversible polymers with relatively high glass transition temperatures \( (T_g) \) are difficult to prepare but very interesting from an application point of view. In this chapter we present a novel reversible thermoset with tunable \( T_g \) based on the chemical modification of aliphatic polyketones (PK) into the corresponding derivatives containing furan (PK-FA) and/or amine (PK-DAP) groups along the backbone. The furan moieties allow thermal setting of the polymers by the Diels-Alder (DA) and retro-DA sequence with bis-maleimide (b-Ma), while the amine moieties allow tuning of the hydrogen bonding density. By this combined approach, it is possible to synthesize well-defined thermosets with a wider \( T_g \) window with respect to PK-FA alone. Indeed, after several heating cycles, the materials showed essentially the mechanical properties of the original materials, even after samples were broken and thermally reshaped. The incorporation of amine moieties at 20 to 60% conversion of the 1,4-dicarbonyl units along the PK-backbone significantly increased the \( T_g \) window from 100 \(^\circ\)C to 185 \(^\circ\)C. However, after each heating cycle the \( T_g \) of the materials, detected as tan (\( \delta \)) in DMTA measurements, continued to increase probably due to imine group formation between unreacted carbonyl and amine groups. Despite this limitation, the studied systems still display reworkability up to three thermal cycles and constitute a proof of principle for the proposed approach, \( i.e. \) the combination of Diels-Alder and hydrogen bonding groups towards higher \( T_g \) materials.

Keywords: Paal-Knorr chemical modification, Diels-Alder reaction, hydrogen bonding interactions, thermoreversible polymers.
2.1 Introduction

Nowadays plastics are ubiquitous in the world as they are used in almost every civil and infrastructural application. As long as new technological developments appear, cheapest products become popular especially for common applications (e.g. plastic bags). However, the cheapest products display in general relatively short life spans, which bring problems with littering, management, disposal and recycling processes [1-6]. In this respect, one of the biggest problems that involve untreated or partially treated plastic wastes is their contribution with hazardous derivatives in aquatic and inland environments [7-10]. Thus, the reuse and management of plastic materials has been attracting an increasing attention especially for the definition of new strategies to reduce environmental problems like global warming [11] and toxicity for human beings [7,12].

Since the development of synthetic polymers like Bakelite (phenol-formaldehydes in 1909) and PE (polyethylene in 1940), many efforts have been undertaken at improving plastic properties, often without taking into account the corresponding environmental implications. From the 1940s, special attention has been paid to the development of cross-linked polymers (e.g. rubbers) [13-17] and thermoset materials [18-21]. The latter are widely used in many applications because of their remarkable mechanical properties such as relatively high modulus (easily tailored for specific applications), solvent resistance and fracture strength. However, as cross-linking is an irreversible process, thermosets cannot be reverted into their un-cross-linked state and their reuse is limited to energy recovery. The latter does not fit into the current sustainable, “cradle-to-cradle” context and does not offer any convenient, future economic perspective as it represents a typical example of recycling while downgrading the corresponding base material [22].

A possible solution to the general problems outlined above resides in the synthesis of reversible cross-linked materials. Several articles have reported the ability of polymer and composite materials to be repaired by different ways, e.g by using low molecular weight molecules imbibed into capsules as healing agent allowing autonomic healing after damage events (extrinsic self-repair) [23-27] or by functionalization of raw non-reworkable polymers, for which, upon external stimuli like heat [28-33] and light [34-36], the recovery of bonding of the functional moieties takes place (intrinsic self-repair). Against this backdrop, the use of covalent, inter-macromolecular Diels-Alder reversible bonds represents a popular choice
when making allowance for the relatively fast kinetics and mild conditions at which this reaction takes place [22, 37, 38]. In particular the furan-maleimide chemistry has been recognized, already from the early developments in this field [30], as a viable option for the reasons outlined above [28, 29, 31-33]. However, most of the works reported in the open literature [22] still rely on lengthy, costly and cumbersome synthetic steps for the preparation of the base materials, i.e. polymeric backbones displaying the presence of Diels-Alder active groups. In this general context, our research group has recently achieved a breakthrough with the preparation of aliphatic polyketones (PK) modified with furan groups and cross-linked with bis-maleimide [32, 33]. This system showed an almost quantitative recovery of thermal and mechanical behavior coupled with the possibility of finely tuning the softening point (as measured by DMTA) in the range between room temperature and 100 °C by simply adjusting the chemical composition of the polymeric backbone and the amount of cross-linking agent used. Furthermore, the modification reaction for the preparation of the basis polymer (i.e. Paal-Knorr modification of aliphatic PK with primary amines) represents a paradigmatic example of simplicity as it proceeds in the bulk (100 °C) with relatively fast kinetics (thus avoiding the use of any solvent or catalyst), with quantitative yields for the amino compound (thus avoiding the necessity of any separation step) and with the formation of water as single by-product [39, 40]. This is very attractive in a general frame of future industrial applications [41]. Nevertheless, up to date, the upper range of softening points has been limited to approximately 100 °C, which represents a clear drawback and limits the application field for these materials. A possible solution to this is represented by the simultaneous presence of different reversible interactions, able to synergistically “reinforce” each other with respect to the thermal stability of the corresponding polymeric chains.

In this work we report our efforts aimed at preparing a thermally reversible polymer network in which Diels-Alder and hydrogen bonds are present. To the best of our knowledge, this represents an absolute novelty in the open literature, at least when taking into account the systematic nature of the study. We start with the conversion of PK into PK-furan/amine derivatives (PK-FA and PK-FA-DAP) by the Paal-Knorr reaction (Figure 2.1). This synthetic strategy should in principle allow achieving full control of the chemical structure of the corresponding polymers, displaying thus a tunable amount of DA and hydrogen bond active groups [32, 33, 39]. We intend to investigate this by elemental analysis (for determination of the conversion), $^1$H-NMR and FT-IR spectroscopy. The prepared polymers are then cross-linked via DA and r-DA sequence with bis-maleimide (Figure 2.2).
Figure 2.1 Schematic representation of polyketone (A), PK functionalized with furfurylamine (PK-FA) (B) and PK-FA functionalized with 1,2 diaminopropane (PK-FA-DAP) (C) by Paal-Knorr reaction.

Figure 2.2 Schematic representation of DA and r-DA sequence of functionalized polyketone PK-FA-DAP cross-linked with bis-maleimide. Red circles indicate hydrogen bonding interactions.

The resulting networks (Figure 2.2) should display the simultaneous presence of both reversible interactions while the corresponding ones with only furan groups rely solely on the
presence of DA inter-macromolecular bonds and, as such, represent the correct reference systems to establish the contribution, if any, of hydrogen bonding interactions. This is checked by Differential Scanning Calorimetry (DSC) and DMTA studies.

2.2 Experimental section

Reagents

The alternating aliphatic polyketone (PK30, MW 2687 Da) presents a total olefin content of 30% of ethylene and 70% of propylene [41, 42]. Furfurylamine was freshly distilled (FA Aldrich, ≥ 99%), while 1,2-diaminopropane (DAP Acros), butylamine (BA, Sigma Aldrich, 99%), (1,1’-(methylenedi-4,1-phenylene)bis-maleimide (Aldrich 95%), chloroform (CHCl₃ Laboratory-Scan, 99.5%), dimethyl sulfoxide (DMSO, Acros, 99.7%) were purchased and used as received.

Polyketone functionalized with Furan and amine pendant groups

The reaction between PK30, furfurylamine and 1,2-diaminopropane were carried out at different ratios between the 1,4-dicarbonyl groups of the polyketone and the primary amine groups of furfurylamine and 1,2-diaminopropane. The molar ratio between the reactants was established as percentage with a maximal carbonyl conversion of 80% as previously reported [32, 33, 39]. The chemical modifications of PK to yield PK with furan groups (PK30-FA), amine groups (PK30-DAP) and a combination thereof (PK30-FA-DAP) were carried out in bulk in a sealed 250 mL round-bottomed glass reactor with a reflux condenser, a U-type anchor impeller, and an oil bath for heating. A single reaction with butylamine (BA) was carried out in order to prepare (see below) an additional reference system. In a typical recipe, PK30 (20 g) was preheated to the liquid state at the employed reaction temperature (110 °C), FA and/or DAP were added dropwise to the reactor in the first 20 min. The stirring speed was set at a constant value of 600 rpm, and the employed reaction time was 4 h [33]. The resulting polymers were frozen with liquid nitrogen, crushed and washed 3 times with deionized Milli-Q water to remove unreacted FA and DAP, if any. After filtering and freeze drying, light-brown polymers were obtained as the final products. The corresponding samples are coded as PK30-amine₁ x₁-amine₂ x₂ with xᵢ being the mol percentage of amine with respect to carbonyl groups in the feed. The carbonyl conversion (X_co) can be calculated by [39,40]:
\[ X_{co} = \frac{(M_{PK30-Conv} \cdot (\%C_{obs} + \%N_{obs}))}{(M_{PK30} + M_{amine} - 2 \cdot M_{water} \cdot (\%C_{exp} + \%N_{exp}))} \cdot 100 \]  (1)

where \( M \) represents the molecular weight of polyketone before (\( M_{PK30} \)) and after conversion (\( M_{PK30\-conv} \)). \( M_{amine} \) represents the molecular weight of furfurylamine, 1,2 diaminopropane and \( M_{water} \) the molecular weight of water. \( C_{obs} \) and \( N_{obs} \) represent the weight percentage of carbon and nitrogen derived from the elemental analysis, while \( C_{exp} \) and \( N_{exp} \) represent the percentage expected for carbon and nitrogen resulting from theoretical calculations. The maximum theoretical value for carbonyl conversion (\( THEO_{Xco} \)) depending on the amine intake (\( g \ amine \)) in the feed can be defined as:

\[ THEO_{Xco} = \frac{g \ amine}{Moles \ PK30 \cdot M_{amine}} \]  (2)

The carbonyl conversion efficiency (\( \eta \)) can be defined as the ratio between the actual conversion and maximum theoretical value.

\[ \eta = \frac{X_{co}}{THEO_{Xco}} \]  (3)

A maximum carbonyl conversion of 80% is assumed on the basis of published data [39, 40].

**Diels-Alder reaction**

The DA reaction of PK30-FA and PK30-FA-DAP (2.5 g) with bis-maleimide were carried out in different ratios between the furan moieties and maleimide groups (Figure 2.2) using chloroform as solvent (≈ 10 wt % polymer based on solvent) in a 100 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was heated to 50 °C for 24 h to form the polymer adduct. After reaction, the cross-linked polymers were dried at 50 °C under vacuum overnight to remove the solvent.

**Characterization**

The elemental analysis was performed with an Euro EA elemental analyzer. \(^{1}\)H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using CDCl\(_3\) as solvent. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000 equipped with a heating stage and temperature controller. The measurements were performed in ATR modality and “Spectrum Beer’s Law” was used as software. DSC analysis was performed on a TA-
Instrument DSC 2920 under N₂ atmosphere. The samples for DSC were weighed (10-17 mg) in an aluminium pan, which was then sealed. The sample was first heated from 0 to 180 °C and then cooling to 0 °C. Four cycles were performed, and the heating and cooling rates were set to 10 °C/min throughout the DSC measurements. The samples for DMTA analysis were prepared by compression moulding of 450 mg of cross-linked PK30-FA / bis-maleimide and PK30-FA-DAP / bis-maleimide into rectangular bars of 6 mm in width, 1 mm in thickness, and 54 mm in length at 150 °C for 30 min under a pressure of 4 MPa, followed by the thermal healing treatment at 50 °C for 24 h in an oven. The DMTA analyses of the bars were conducted on a rheometrics scientific solid analyzer (RSA II) under an air environment using the dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C/min.

2.3 Results and discussion

The reactions between PK30 and furfuryl amine and/or 1,2 diaminopropane were carried out according to different molar ratios (Table 2.1).

**Table 2.1** Conversion of PK30 in presence of different ratios of furfurylamine (FA) and 1,2 diaminopropane (DAP).

<table>
<thead>
<tr>
<th>Run</th>
<th>X_{CO} (%) a</th>
<th>η (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-BA80</td>
<td>78</td>
<td>98</td>
</tr>
<tr>
<td>PK30-DAP20</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>PK30-DAP40</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>PK30-DAP60</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>PK30-DAP80</td>
<td>79</td>
<td>97</td>
</tr>
<tr>
<td>PK30-FA20</td>
<td>19</td>
<td>99</td>
</tr>
<tr>
<td>PK30-FA40</td>
<td>39</td>
<td>99</td>
</tr>
<tr>
<td>PK30-FA60</td>
<td>58</td>
<td>98</td>
</tr>
<tr>
<td>PK30-FA80</td>
<td>76</td>
<td>96</td>
</tr>
<tr>
<td>PK30-FA60-DAP20</td>
<td>78</td>
<td>98</td>
</tr>
<tr>
<td>PK30-FA40-DAP40</td>
<td>77</td>
<td>96</td>
</tr>
<tr>
<td>PK30-FA20-DAP60</td>
<td>79</td>
<td>99</td>
</tr>
</tbody>
</table>

a % conversion of carbonyl groups. b η conversion efficiency.

All samples with combined groups, *i.e.* the PK30-FA-DAP series, display a total carbonyl conversion of about 80%, *i.e.* a quantitative one. Indeed, in terms of conversion efficiency, all used amines display values around 100%, thus testifying the easiness of the reaction as well
as its quantitative yield for the amino compound. Slightly lower η values are obtained for FA, in agreement with the sensitivity of this reaction to steric hindrance [39, 43].

The solubility of all obtained polymers in common organic solvents (e.g. CHCl₃, acetone and DMSO) as well as previous literature on the Paal-Knorr reaction and its sensitivity to steric hindrance [39] indicate that only the less hindered amino group of 1,2-DAP actually reacts with the PK backbone and thus no cross-linked product is formed. Furthermore, ¹³C-NMR spectra (not shown for brevity) lack any indication of additional imines (Schiff bases), which should be formed upon cross-linking at such high level of carbonyl conversion. The ¹H-NMR spectra of the polymer with different pendants groups are displayed in Figure 2.3.

Figure 2.3A (reaction of PK30 with FA) shows the formation of pyrrole groups at 5.8 ppm, the presence of CH₂ units attached between the pyrrole and furan groups at 4.9 ppm and the protons of furan moieties at 7.3, 6.2 and 5.9 ppm [32,33]. In a similar way, Figure 2.3B (reaction of PK30 with DAP) displays the formation of pyrrole groups at 5.8 ppm, the presence of CH₂ attached to the pyrrole groups at 3.6 ppm, the CH in β position at 3.2 ppm [39]. Finally, Figure 2.3C is showing the conversion of PK30 with both pendant groups. A quantitative analysis of the spectra is hindered by the broad character of many peaks as well as by their overlap for the PK30-FA-DAP. Nevertheless, at least on a qualitative level, this agrees with the formation of the desired structure. Furthermore, spectral data obtained by FT-IR analysis corroborate the ¹H-NMR results with the appearance of pyrrole rings at 3114 and 1597 cm⁻¹ and the furan moieties at 3150 and 737 cm⁻¹ (Figure 2.4) [44].

As expected, when going form PK30-FA80 to PK30-FA20-DAP60 through all intermediate composition values (i.e. from A to D in Figure 2.4) the typical furan adsorption peaks (vide supra) decrease in intensity while the one assigned to the pyrrole rings remain unchanged. This is in agreement with the elemental analysis data showing a total (constant) conversion of 80% for the PK30-FA-DAP series and thus a constant amount of pyrrole groups along the polymer backbone.

All prepared polymers (before cross-linking) were characterized by DSC analysis (Figure 2.5). Polymers with only one component (either FA or DAP) display a monotonous increase of the Tₓ with the amine conversion (Figure 2.5A). This is in agreement with the increased rigidity of the backbone with increasing amount of pyrrole groups.
Figure 2.3 $^1$H-NMR spectra of (A) PK30 and furfurylamine before (I) and after (II) reaction; (B) PK30 and 1,2 diaminopropane before (I) and after (II) reaction; (C) PK30 alone (I), PK30-furan functionalized (II) and PK30-furan after reaction with 1,2 diaminopropane (III).

Moreover, PK functionalized with amino groups (PK-DAP) systematically displays (at equal conversion values) significantly higher $T_g$ values than the one modified with furan ones (PK-FA). This testifies the relevant contribution (differences are up to 90°C) of hydrogen bonding interactions in determining the thermal properties, thus confirming the general idea of this study (vide supra). Moreover, if one takes into account also the $T_g$ value for PK30-BA80
(14°C), *i.e.* the polymer modified with butylamine (displaying the same backbone as PK30-DAP80 but without interacting side chains), it is possible to highlight also the (slight) contribution of the furan groups (probably via π-stacking interactions) in increasing the $T_g$ value of the original polyketone.

![Figure 2.4 FT-IR spectra](image)

**Figure 2.4** FT-IR spectra of PK30 modified with furfurylamine (PK30-FA) and PK30-FA conversion with 1,2 diaminopropane (PK30-FA-DAP) at different ratios.

As expected, samples of the PK30-FA-DAP series (thus displaying the presence of both interactions) show $T_g$ values intermediate between the ones of the two reference compounds (PK-FA80 and PK-DAP80) at the same total conversion value (Figure 2.5B). All DSC data clearly demonstrate, even before cross-linking, the remarkable versatility of the employed synthetic approach in yielding several different polymeric systems with tuneable thermal behaviour as function of composition.

The cross-linking reactions of PK30-FA and PK30-FA-DAP with bis-maleimide were carried out at 50 °C for 24 h. As previously reported [33], IR spectroscopy is useful to monitor the DA cycloaddition reaction through the spectral band of C-O stretching around 1000-1300 cm$^{-1}$. Figure 2.6 shows FT-IR spectral results for the reaction of PK30-FA and PK30-FA-DAP.
with bis-maleimide at different molar ratios between furan and maleimide groups. The band centred around 1180 cm\(^{-1}\) corresponds with the C-O-C ether peak. Its intensity increases with the molar ratio between furan and maleimide groups, thus testifying the occurrence of the Diels-Alder reaction. In analogy with previous reports [33], the molar ratio between furan and maleimide were systematically changed (Table 2.2).

![Figure 2.5 T\(_g\) (as measured by DSC) of PK30 as a function of conversion percentage with furfurylamine or diaminopropane (A) and as function of different furfurylamine / diaminopropane ratios at 80\% total conversion (B).](image)

The mechanical behaviour of all prepared samples (as solid bars) was tested by DMTA at three heating cycles. The corresponding T\(_g\) values (taken as peak of tan (\(\delta\)) in the corresponding DMTA curves) increase with the furan/maleimide molar ratio (for every series), as expected on the basis of the corresponding network density. More importantly, if
one compares materials with the same total carbonyl conversion but displaying the presence of different groups along the backbone (e.g. PK30-FA80, PK30-FA60-DAP20, PK30-FA40-DAP40, PK30-FA20-DAP60), it is clear that the corresponding $T_g$ increases with the relative amount of amino groups (i.e. hydrogen bonding interactions) with respect to the furan ones (i.e. DA adduct).

**Figure 2.6** FT-IR spectra of PK30 functionalized with furfurylamine (PK30-FA80) (A) and 1,2 diaminopropane (PK30-FA20DAP60) (B) cross-linked at different FA/Ma ratios. Bands normalized at 2887 cm$^{-1}$ (C-H stretch).

The trend is not linear with composition (or at least it does not seem to follow a linear pattern) since hydrogen bonding between amino groups and the carbonyls on the bis-maleimide compound might also take place and thus decrease the amount of available $-\text{NH}_2$ groups. Moreover, the recovery of mechanical properties (modulus in this case) seems to be
almost quantitative for both PK30-FA (Figure 2.7A) and PK30-FA-DAP (Figure 2.7B, for brevity only one sample is shown).

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Ratio Fa/Ma</th>
<th>$T_g$ (°C)</th>
<th>$\Delta T_g$ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-FA80</td>
<td>1 / 0.25</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>PK30-FA80</td>
<td>1 / 0.5</td>
<td>111</td>
<td>0</td>
</tr>
<tr>
<td>PK30-FA80</td>
<td>1 / 0.75</td>
<td>130</td>
<td>0</td>
</tr>
<tr>
<td>PK30-FA80</td>
<td>1 / 1</td>
<td>140</td>
<td>0</td>
</tr>
<tr>
<td>PK30-FA60-DAP20</td>
<td>1 / 0.25</td>
<td>95</td>
<td>0</td>
</tr>
<tr>
<td>PK30-FA60-DAP20</td>
<td>1 / 0.5</td>
<td>125</td>
<td>8</td>
</tr>
<tr>
<td>PK30-FA60-DAP20</td>
<td>1 / 0.75</td>
<td>135</td>
<td>11</td>
</tr>
<tr>
<td>PK30-FA60-DAP20</td>
<td>1 / 1</td>
<td>161</td>
<td>21</td>
</tr>
<tr>
<td>PK30-FA40-DAP40</td>
<td>1 / 0.25</td>
<td>125</td>
<td>12</td>
</tr>
<tr>
<td>PK30-FA40-DAP40</td>
<td>1 / 0.5</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>PK30-FA40-DAP40</td>
<td>1 / 0.75</td>
<td>159</td>
<td>21</td>
</tr>
<tr>
<td>PK30-FA40-DAP40</td>
<td>1 / 1</td>
<td>183</td>
<td>32</td>
</tr>
<tr>
<td>PK30-FA20-DAP60</td>
<td>1 / 0.25</td>
<td>129</td>
<td>n.d.</td>
</tr>
<tr>
<td>PK30-FA20-DAP60</td>
<td>1 / 0.5</td>
<td>126</td>
<td>13</td>
</tr>
<tr>
<td>PK30-FA20-DAP60</td>
<td>1 / 0.75</td>
<td>155</td>
<td>20</td>
</tr>
<tr>
<td>PK30-FA20-DAP60</td>
<td>1 / 1</td>
<td>185</td>
<td>40</td>
</tr>
</tbody>
</table>

* $T_g$ difference between the 1° and 3° heating cycle. Data obtained by DMTA measurements.

However, samples displaying the presence of both interactions (PK30-FA-DAP) show a systematic increase in the softening temperature (see Figure 2.7B for an example) upon thermal cycling. This phenomenon is systematic and can result (Table 2.2) in differences up to 40 °C between the $T_g$ measured during the last (third) and first DMTA cycle.

Although this does not seem to affect the mechanical properties (modulus) and their recovery in a relevant way, the reasons for such behaviour were further investigated. The increase in the softening temperature could suggest an inter-polymeric conformational re-arrangement or a side reaction between the unreacted functional groups as an effect of temperature exposure. To clarify this point, every sample (after the three heating cycles) was analysed by FTIR.
The rather complicated absorption patterns did not allow a direct analysis and a deconvolution procedure was thus applied. In particular (Figure 2.8A) the absorption in the carbonyl region was deconvoluted yielding, as first result, the presence of an imine (Schiff base) absorption [45] at around 1640 cm$^{-1}$. This suggests the possible reaction of the free amino groups with unreacted carbonyls along the polymer backbone, which should be faster and more prominent with increasing amount of amino groups along the backbone. This can be clarified when plotting (Figure 2.8B) the ratio between the peak area at 1640 cm$^{-1}$ (imine group) with the one at 1703 cm$^{-1}$ (carbonyl group) as function of the amino group intake. It is clear (not shown for brevity) how this ratio does not change when amino groups are not present in the system, thus proving the lack of any side reactions. On the other hand, if amino
groups are present in the systems such ratio significantly increases (Figure 2.8B) after the DMTA cycles (with respect to the original material), with the magnitude of the difference also increasing as function of the DAP intake.

**Figure 2.8** (A) FT-IR deconvolution spectra of PK30-FA40-DAP40 cross-linked with bis-maleimide evaluated after three DMTA cycles ($R^2 = 0.98$). (B) Ratio between imine region band (1640 cm$^{-1}$) and carbonyl band (1703 cm$^{-1}$) of PK30-FA-DAP/bis-maleimide (before and after 3 DMTA cycles) as a function of DAP moieties intake. Data obtained from deconvolution of FT-IR spectra.

The presented data clearly show that the presence of amino groups is, for this particular system, not a full advantage. Despite the clear increase in softening point and the still almost quantitative recovery of elastic modulus during the thermal cycles, the formation of permanent (*i.e.* not reversible in the solid state) cross-linking points through imine formation
might seriously hinder full reworkability of the prepared materials (at least after more than three heating cycles). In this context, the use of other hydrogen bonding groups, not reactive towards carbonyl ones, might represent a more viable option and is currently under investigation.

2.4 Conclusions

A new class of polymeric materials, bearing Diels-Alder as well as hydrogen bonding active groups along the backbone, has been successfully synthesized by chemical modification of aliphatic polyketones. The employed synthetic strategy (Paal-Knorr reaction with primary amines) allows easy preparation of these materials with a series of general advantages related to this kind of polyketone modification. The thermal properties of the polymers, even before cross-linking, testify the relevant contribution of hydrogen bonding interactions to the final glass transition temperature values. Furthermore, the prepared polymers, after cross-linking with a bis-maleimide, clearly showed improved $T_g$ values with respect to the respective counterparts containing only furan groups. From an applicative point of view, this significantly extends the upper limit of available $T_g$ values for these materials from 100 °C (as reported in previous works) up to 185 °C without any significant effect (or in any case very little) on the recovery of mechanical properties (i.e. modulus) after three thermal cycles. However, a significant shift in the $T_g$ values (as measured by DMTA) can be observed during the thermal cycles. This has been preliminarily attributed to the side reaction of the free amine groups with the unreacted carbonyls along the polymeric backbone. Such unwanted feature renders the proposed system not entirely optimal, although significantly better than previously reported ones, in terms of end-product reworkability. The incorporation of hydrogen bonding groups not able to react with the free carbonyl groups is currently under investigation, as it might pave the way towards more efficient systems.

2.5 References

3 Intrinsic self-healing thermosets through covalent and hydrogen bonding interactions

**Abstract**: The intrinsic self-healing ability of polyketone (PK) chemically modified into furan and/or OH groups containing derivatives is presented. Polymers bearing different ratios of both functional groups were cross-linked via furan / bis-maleimide (Diels-Alder adducts) and hydrogen bonding interactions (aliphatic and aromatic OH groups). The resulting thermosets display tuneable softening points (peak of tan (δ)) from 90 to 137 °C as established by DMTA. It is found that the cross-linked system containing only furan groups shows the highest softening temperature. On the other hand, systems displaying the combination of Diels-Alder adducts and hydrogen bonding (up to 60 mol % of -OH groups) do not show any change in modulus between heating cycles (i.e. factually a quantitative recovery of the mechanical behaviour). It is believed that the novelty of these tuneable thermosets can offer significant advantages over conventional reversible covalent systems. The synergistic reinforcement of both interactions resists multiple heating/healing cycles without any loss of mechanical properties even for thermally healed broken samples.

**Keywords**: Paal-Knorr chemical modification, Diels-Alder reaction, Hydrogen bonding interactions, tuneable self-healing thermoset, recycling.
3.1 Introduction

Over the last few decades, researchers working on the design and optimization of plastic materials have reported considerable improvements (e.g. in mechanical properties of recycled materials) often stimulated by societal driven demands in terms of sustainability, enhancement of material quality and value-add services [1, 2]. However, despite all the efforts, it is widely recognized that plastic recycling is still facing major problems regarding collection, separation, cleaning, processing chemistry and flow markets for recycled products [3-6].

As an attempt for improvements in this matter, the European Commission has categorized the waste treatment according to the most environmentally favourable strategies. The “waste hierarchy” establishes as priority the prevention follows by the reuse and recycling of waste, while the less favourable strategies are the recovery and disposal [7]. In the particular case of plastics, suitable materials for recycling are subjected to the availability of treatment technology and markets [8, 9]. For instance, the most used procedures for thermoplastics recycling are the physical and chemical approaches. The physical recycling is realized by the grinding and re-melting of thermoplastics to produce a material with equal, similar or completely different properties compared to the original one. On the other hand, the chemical recycling turns thermoplastics into monomers or oligomers (by the addition of chemical additives and processing conditions) to be used as raw materials for the production of new polymers [10].

Thermosets unlike thermoplastics, cannot be recycled by using the above mentioned approaches (e.g. re-melted / re-shaped or chemical reduction to monomers) since they degrade or decompose. In this context, (thermally) reversible thermoset materials represent an accessible solution due to their remarkable ability of being mended and recycled (according to a “cradle to cradle” approach) in order to prolong their use after their first service life [11]. Several scientific articles have reported the ability of thermoset polymers to be repaired in different ways. These include the incorporation of low molecular weight additives in the form of capsules as healing agent after damage events (extrinsic self-repair) [12-16], but also the functionalization of raw non-reworkable polymers that can heal cracks as a consequence of external stimuli like heat [17-20] and light [21-25] (intrinsic self-repair). The last approach relies on the chemical modification of the base polymer with functional
groups able to undergo a reversible reaction. Diels-Alder or hydrogen bonding active groups are indeed often employed to prepare polymer networks with thermally reversible properties [26, 27]. Therefore, in a fracture event, the healing process can be performed by the combination of covalent (Diels-Alder) and or non-covalent (H-bonds) reversible interactions. It is ideal as the intrinsic self-healing ability (i.e. bonds reconnection) of both functional groups plays a crucial role in supporting the recovery of the network (e.g. dimensional stability) at different levels of energy (i.e. complementary reinforcement of chemical and physical interactions). Therefore, the healing process can be achieved under different conditions (e.g. temperature) just by controlling the ratio between the introduced functional groups. These advantages have recently triggered the research on thermoset systems with tuneable chemical reversibility and mechanical properties (e.g. polymers containing reversible [20, 26, 28, 29] and non-reversible [30-32] covalent interactions in combination with hydrogen bonding). However, the design of this kind of materials still faces problems in terms of lengthy, costly and cumbersome synthetic steps, thus hindering any application at industrial scale.

We recently reported on the novel thermally self-healing properties of polymer networks containing reversible covalent and non-covalent interactions based on aliphatic polyketones [20, 33]. In order to prepare the target materials, we started modifying alternating aliphatic polyketone (PK) into new polymers by using the Paal-Knorr reaction, i.e. the chemical modification of the di-carbonyl arrangement of PK into pyrrole groups bearing furan or amine active groups [20]. This synthetic pathway offers several advantages like high yield under relatively mild condition (100 °C) and reaction kinetics (4 h) even without any catalyst, with water as the only by-product. Subsequently, the modified PK was covalently cross-linked through the Diels-Alder (DA) reaction by using bis-maleimide. The simultaneous presence in the modified polymers of both interactions (H-bonding and DA adducts) resulted in networks with softening points from 100 to 185 °C. Remarkably, the materials retained quantitative modulus values after multiple heating-healing cycles. However, they also displayed an increase in the softening point between cycles, which was ascribed to the formation of irreversible cross-linking points via the reaction of the pendant amine groups with the unreacted carbonyls along the backbone [20]. In order to overcome this drawback, this work is focused on preparing tuneable reversible thermosets through the synergistic cooperation of covalent and non-covalent interactions. These materials should then be able to display reversible properties after several heating/healing and recycling cycles. In principle,
this can be achieved by using OH functional groups (instead of amino ones) as hydrogen bonding active moieties, thus avoiding any side reaction with the unreacted carbonyls along the backbone. In order to establish more clearly the role of the OH-groups, reference polymers displaying the same pyrrolic backbone of the target ones were functionalized with less reactive moieties without OH groups.

After modification, the polymers are covalently cross-linked via furan/maleimide Diels-Alder and hydrogen bonds. The thermal and mechanical behaviour is then studied by differential scanning calorimetry DSC and dynamic mechanical thermal analysis (DMTA) to determine the reversibility, rework-ability and intrinsic self-healing ability of the thermoset polymers.

3.2 Experimental section

Reagents

The alternating aliphatic polyketone (PK30, MW 2687 Da) presents a total olefin content of 30% of ethylene and 70% of propylene [34, 35]. The polymer presents a 43% of carbonyl content on the basis of the total molecular weight. Furfurylamine (Fu) was freshly distilled (Aldrich, ≥ 99%). 3-amino-1-propanol (Ap) (Acros, The Netherland), 2-(4-hydroxyphenyl)ethylamine (tyramine Ty) (Sigma Aldrich 99%), 2,5-hexanedione (Sigma Aldrich 98%), butylamine (Ba) (Sigma Aldrich 99%) benzylamine (Bea) (Sigma Aldrich 99%), 1-Propanol, Milli-Q water, (1,1-(methylenedi-4,1-phenylene) bis-maleimide (b-Ma) (Sigma Aldrich 95%), chloroform (CHCl3 Laboratory-Scan, 99.5%), were purchased and used as received. Deuterated dimethylsulfoxide (DMSO-d6, Sigma Aldrich, ≥99 atom%) was used as solvent for 1H-NMR measurements.

Model component reaction

Model reactions between stoichiometric amounts of 2,5-hexanedione (8.7 mmol) with either furfurylamine (previously reported by our group [36]), 3-amino-1-propanol (0.65 g) or tyramine (1.2 g) were carried out in order to identify the presence of any side product. The reactants were poured into a flask provided with a reflux condenser and transferred to the microwave apparatus. The reactions were performed at 100 °C (200 watts) for two hours in bulk in the case of 2,5-hexanedione with 3-amino-1-propanol and using 1-propanol as solvent (10 wt.%) in the case of 2,5-hexanedione with tyramine. Thereafter, the organic solvent was
removed in a vacuum oven at 50 °C for 24 h and the by-product (H₂O) was removed in a freeze dryer for 72 hours.

**Polyketone modification**

The chemical modification of PK30 was performed by two different heating methods (1 conventional oil bath and 2 microwave oven). In both methods, different molar ratios between 1,4-dicarbonyl of PK30 and amine compounds were used. PK30-Fu and PK30-Fu-Ap were prepared in a conventional oil bath as well as the reference polymers PK30-Ba and PK30-Bea, while PK-Fu and PK-Fu-Ty by using the microwave oven.

In the case of 1, the reactions were carried out in bulk in a sealed 250 mL round-bottomed glass reactor with a reflux condenser, a U-type anchor impeller, and an oil bath for heating. After 60 g of PK30 were preheated to a liquid state at 100 °C, the amine compounds furfurylamine and/or 3-amino-1-propanol (butylamine or benzylamine for reference polymers) were added dropwise to the reactor during the first 20 min (mmol equivalent to 20 – 80 % aimed conversion). The stirring speed was set at a constant value of 600 rpm and the reaction time was set at 4 h.

Procedure number 2 is employed to reduce the reaction time for the chemical modification of PK30 into polymers bearing Fu and aromatic-OH groups [37]. In a typical experiment, a mixture of polymer (4.0 g PK30) with furfurylamine and/or tyramine (mmol equivalent to 35 – 80 % aimed conversion) was pre-dissolved in 1-propanol (≈ 10 wt.% of polymer) and then poured into a flask provided with a reflux and transferred to the microwave apparatus. The microwave power was set at 200 Watts to keep a constant temperature of 100 °C for 2 hours. After reaction, the solvent was removed using rotary evaporation. Finally, the products were dried under vacuum at 50 °C for 24 h.

In both procedures, the resulting polymers were frozen with liquid nitrogen, crushed to powdery samples and washed three times with deionized Milli-Q water to remove unreacted amine compounds, if any. After filtering and freeze drying, light-brown polymers were obtained as final products. The carbonyl conversion (C<sub>co</sub>) of PK30 can be calculated by:

\[ C_{co} = \frac{y}{y+x} \cdot 100 \]  

(1)
where \( x \) and \( y \) represent the moles of di-ketone and pyrrolic units after conversion, respectively. \( y \) can be calculated as follows:

\[
y = \frac{N}{A_{m(N)}}
\]  

(2)

Where \( N \) represents the grams of nitrogen in the product according to elemental analysis and \( A_{m(N)} \) represents the atomic mass of nitrogen. \( x \) can be calculated as follows:

\[
g_{\text{prod}} = x \cdot M_{w}^{pk} + y \cdot M_{w}^{y}
\]  

(3)

where \( g_{\text{prod}} \) represents the grams of the final product after conversion, \( M_{w}^{y} \) the molecular weight of the pyrrolic unit (i.e. pyrrolic units bearing either Fu, OH or both functional groups) and \( M_{w}^{pk} \) the molecular weight of the 1,4 di-ketone unit. Then we can conclude that:

\[
x = \frac{g_{\text{prod}} - y \cdot M_{w}^{y}}{M_{w}^{pk}}
\]  

(4)

The conversion efficiency \( \eta \) can be defined as the ratio between the final carbonyl conversion \( C_{co} \) and the targeted one according to the amount of polymer and amine compounds provided in the feed \( (C_{co}^{\text{feed}}) \):

\[
\eta = \frac{C_{co}}{C_{co}^{\text{feed}}} \cdot 100
\]  

(5)

The \( C_{co}^{\text{feed}} \) is calculated as follow:

\[
C_{co}^{\text{feed}} = \frac{\text{Molamine}}{\text{Mol}_{PK30}} \cdot 100
\]  

(6)

with \( \text{Molamine} \) representing the moles of amine compounds and \( \text{Mol}_{PK30} \) the moles of di-carbonyl units in the feed.

**Diels-Alder reaction**

The DA reaction of PK30-Fu and PK30-Fu-OH (2.0 gr) with bis-maleimide was carried out in a ratio 1:1 between the furan moiety and the maleimide group using chloroform as solvent (\( \approx 10 \) wt.% of polymer) in a 100 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was heated up to 50 °C for 24 h to form the DA adducts. After reaction, the cross-linked polymers were dried at 50 °C under vacuum overnight to remove the solvent.
**Characterization**

The elemental analysis was performed using an Euro EA elemental analyzer. $^1$H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using DMSO-d$_6$ as solvent (residual resonance at 2.5 ppm). FT-IR spectra were recorded using a Perkin-Elmer Spectrum 2000. The samples (pellets) were prepared by mixing potassium bromide (KBr) with the polymers at (1.5 wt.%). The pills were then kept in an oven for 24 hours at 50 °C to remove residual water. DSC analysis was performed on a TA-Instrument DSC 2920 under N$_2$ atmosphere. The samples for DSC were weighed (10-17 mg) in an aluminium pan, which was then sealed. The samples were first heated from 0 to 180 °C and then cooled to 0 °C. Four cycles were performed at 10 °C/min scanning rates. GPC measurements were performed with a HP1100 Hewlett-Packard to evaluate possible side reactions of the polymers during the modification step, if any. The equipment consists of three 300 x 7.5 mm PLgel 3 μm MIXED-E columns in series and a GBC LC 1240 IR detector. The samples were dissolved in THF at a concentration of 1 mg/mL. THF was used as eluent at a flow rate of 1 mL/min at a temperature of 40 °C. The calibration curve was realized using polystyrene as standard and the data were determined using PSS WinGPC software. The samples for DMTA analysis were prepared by compression molding of 500 mg of cross-linked PK30-Fu / Bis-maleimide and PK30-Fu-OH / Bis-maleimide into rectangular bars of 6 mm in width, 1 mm in thickness, and 54 mm in length at 150 °C for 30 min under a pressure of 40 bar. The samples were then kept in an oven at 50 °C for 24 h aimed at thermal healing treatment. The DMTA analysis of the bars was conducted on a Rheometrics scientific solid analyzer (RSA II) under an air environment using the dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C/min.

### 3.3 Results and discussion

**Model component Paal-Knorr reaction**

Model reactions of 2,5-hexanedione (i.e. representative for the di-carbonyl moieties along the PK30 backbone) with aliphatic and aromatic amines were performed. The present Paal-Knorr reaction resulted in the formation of a pyrrole group, ultimately yielding pyrrole-furane [36] and pyrrole-OH derivatives (see Figure 3.1 for H-NMR spectra). In Figure 3.1A it is possible to notice the signal of protons associated to the pyrrole ring at 5.6 ppm, the presence of CH$_2$ units at 1.6, 3.4 and 3.8 ppm and the proton signal at 4.6 corresponding to the OH group. In a
similar way, Figure 3.1B displays the proton signals associated to the pyrrole ring at 5.6 ppm, the presence of CH$_2$ units at 2.7 and 3.8 ppm, the proton signals associated to the aromatic ring at 6.6 and 6.9 ppm and the proton signal corresponding to the OH group at 9.2. In both cases, no relevant by-products are observed and, in particular, no evidence is found for a possible reaction between the –OH and carbonyl groups.

![Figure 3.1](image)

**Figure 3.1** $^1$H-NMR spectra of model compound reaction between 2,5-hexanedione and 3-amino-1-propanol A and tyramine B. The peak at 3.3 ppm can be assigned to residual water.

**Paal-Knorr reaction of PK30**

The aim of this work is the preparation of thermo-reversible polymer networks by combining reversible covalent bonding (DA and r-DA sequence) using PK-furan derivatives together with OH groups. We started with the conversion of PK into the PK-Furan-OH (*i.e.* aliphatic or aromatic OH derivatives) by Paal-Knorr reaction by using a mixture of the corresponding amino compounds (Figure 3.2).

![Figure 3.2](image)

**Figure 3.2** Schematic representation of polyketone PK functionalized with aliphatic and aromatic amines by Paal-Knorr reaction.

Since the amine conversion is practically quantitative in this reaction [20, 36], this easily allows (in principle) the preparation of materials characterized by different conversion values
of carbonyl groups. The reactions between PK30 and aliphatic / aromatic amine compounds were carried out according to different molar ratios as expressed in the sample nomenclature (Table 3.1). The corresponding samples are coded as PK30-Fu \( X_1 \)-OH \( X_2 \) with \( x_i \) being the mol percentage of amine with respect to carbonyl groups in the feed while OH represents a common symbol for 3-amine-1-propanol (Ap) or tyramine (Ty).

Table 3.1 Experimental conditions and results of the chemical modification of PK30 using different ratios between aliphatic and aromatic amine compounds (\( X_{NH_2} \)).

<table>
<thead>
<tr>
<th>Oil bath</th>
<th>( X_{NH_2}/C=0 )</th>
<th>( X_{NH_2} ) (moles)</th>
<th>( C_{CO}^a ) (%)</th>
<th>( \eta^b ) (%)</th>
<th>Microwave</th>
<th>( X_{NH_2}/C=0 )</th>
<th>( X_{NH_2} ) (moles)</th>
<th>( C_{CO}^a ) (%)</th>
<th>( \eta^b ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-Ba80*</td>
<td>0.8</td>
<td>0.365</td>
<td>78</td>
<td>98</td>
<td>PK30-Bea80*</td>
<td>0.8</td>
<td>0.024</td>
<td>69</td>
<td>86</td>
</tr>
<tr>
<td>PK30-Fu20</td>
<td>0.2</td>
<td>0.091</td>
<td>19</td>
<td>99</td>
<td>PK30-Fu80</td>
<td>0.8</td>
<td>0.024</td>
<td>68</td>
<td>85</td>
</tr>
<tr>
<td>PK30-Fu40</td>
<td>0.4</td>
<td>0.182</td>
<td>39</td>
<td>99</td>
<td>PK30-Ty35</td>
<td>0.35</td>
<td>0.011</td>
<td>34</td>
<td>97</td>
</tr>
<tr>
<td>PK30-Fu60</td>
<td>0.6</td>
<td>0.274</td>
<td>58</td>
<td>98</td>
<td>PK30-Ty50</td>
<td>0.5</td>
<td>0.015</td>
<td>49</td>
<td>98</td>
</tr>
<tr>
<td>PK30-Fu80</td>
<td>0.8</td>
<td>0.365</td>
<td>76</td>
<td>96</td>
<td>PK30-Ty65</td>
<td>0.65</td>
<td>0.020</td>
<td>63</td>
<td>97</td>
</tr>
<tr>
<td>PK30-Ap20</td>
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<td>0.091</td>
<td>15</td>
<td>75</td>
<td>PK30-Ty80</td>
<td>0.8</td>
<td>0.024</td>
<td>76</td>
<td>95</td>
</tr>
<tr>
<td>PK30-Ap40</td>
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<td>0.182</td>
<td>36</td>
<td>90</td>
<td>PK30-Fu65-Ty15</td>
<td>0.8</td>
<td>0.024</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>PK30-Ap60</td>
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<td>0.274</td>
<td>57</td>
<td>95</td>
<td>PK30-Fu50-Ty30</td>
<td>0.8</td>
<td>0.024</td>
<td>67</td>
<td>83</td>
</tr>
<tr>
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<td>79</td>
<td>99</td>
<td>PK30-Fu35-Ty45</td>
<td>0.8</td>
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<td>73</td>
<td>91</td>
</tr>
<tr>
<td>PK30-Fu20-Ap60</td>
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<td>0.365</td>
<td>77</td>
<td>96</td>
<td>PK30-Fu15-Ty65</td>
<td>0.8</td>
<td>0.024</td>
<td>73</td>
<td>91</td>
</tr>
<tr>
<td>PK30-Fu40-Ap40</td>
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<td>0.365</td>
<td>78</td>
<td>97</td>
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<tr>
<td>PK30-Fu60-Ap20</td>
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<td>78</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \) % conversion of carbonyl groups \( C_{CO} \), \( b \) \( \eta \) conversion efficiency.*reference samples: PK30-Ba (butylamine) and PK30-Bea (benzylamine) same polymer structure but not bearing active functional Fu (furan) or OH (propanol, phenol) groups

The obtained results (Table 3.1) include the carbonyl conversion (\( C_{CO} \), as measured experimentally) and the relative efficiency for the main conversion (\( \eta \)). Indeed, in terms of conversion efficiency, almost all used amines display values around 100%, thus testifying the easiness of the reaction as well as its quantitative yield [20, 36]. Moreover, the reported data in Table 3.1 confirm that the use of microwaves can significantly shorten the reaction time with no detrimental effect on the conversion values [20, 36, 38, 39]. However, minor
detrimental effects were observed on the molecular weight of polymers modified with only tyramine according to GPC data (Table 3.2).

**Table 3.2** GPC measurements of PK30 modified with Butilamine (Ba), benzylamine (Bea), 3-amino-1-propanol (Ap), tyramine (Ty) and furfurylamine (Fu) at a maximal 80% of conversion and different ratios between Fu and amine compounds bearing OH groups (Ap and Ty).

<table>
<thead>
<tr>
<th>Run</th>
<th>Mn (x 10^3)</th>
<th>Mw (x 10^3)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK30-Ba80</td>
<td>3.4</td>
<td>6.1</td>
<td>1.8</td>
</tr>
<tr>
<td>PK30-Bea80</td>
<td>2.9</td>
<td>6.5</td>
<td>2.2</td>
</tr>
<tr>
<td>PK30-Ap80</td>
<td>2.7</td>
<td>6.2</td>
<td>2.3</td>
</tr>
<tr>
<td>PK30-Ty35</td>
<td>2.8</td>
<td>6.7</td>
<td>2.4</td>
</tr>
<tr>
<td>PK30-Ty50</td>
<td>2.6</td>
<td>5.5</td>
<td>2.1</td>
</tr>
<tr>
<td>PK30-Ty65</td>
<td>2.5</td>
<td>4.7</td>
<td>1.9</td>
</tr>
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<td>PK30-Ty80</td>
<td>2.0</td>
<td>3.3</td>
<td>1.7</td>
</tr>
<tr>
<td>PK30-Fu80</td>
<td>2.8</td>
<td>6.5</td>
<td>2.3</td>
</tr>
<tr>
<td>PK30-Fu60-Ap20</td>
<td>3.3</td>
<td>6.4</td>
<td>1.9</td>
</tr>
<tr>
<td>PK30-Fu40-Ap40</td>
<td>2.9</td>
<td>6.1</td>
<td>2.0</td>
</tr>
<tr>
<td>PK30-Fu20-Ap60</td>
<td>2.8</td>
<td>5.8</td>
<td>2.0</td>
</tr>
<tr>
<td>PK30-Fu65-Ty15</td>
<td>3.0</td>
<td>7.0</td>
<td>2.3</td>
</tr>
<tr>
<td>PK30-Fu50-Ty30</td>
<td>3.1</td>
<td>7.1</td>
<td>2.3</td>
</tr>
<tr>
<td>PK30-Fu35-Ty45</td>
<td>3.1</td>
<td>6.5</td>
<td>2.1</td>
</tr>
<tr>
<td>PK30-Fu15-Ty65</td>
<td>2.9</td>
<td>5.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Besides, slightly lower η values are obtained for PK30-Fu-Ty when the concentration of Fu is increased, in agreement with the sensitivity of this reaction to steric hindrance [39, 40]. The \(^1\)H-NMR spectra of the polymers bearing different ratios of pendant groups are displayed in Figure 3.3. As mentioned earlier, model compounds can be used as simple representations of complex polymeric systems. In the case of Figure 3.3, the overlapping and broad character of many peaks was easily overcome using the information obtained from the model compounds. Figure 3.3A shows signals that belong to protons associated to pyrrole rings at 5.6 ppm, the presence of CH\(_2\) units attached to the pyrrol groups in the OH moiety at 3.3 and 3.7 ppm and the proton signal of OH groups at 4.6 ppm. In a similar way, the presence of CH\(_2\) unit between the pyrrol and furan group is noticed at 4.9 ppm and proton signals of furan moieties at 6.1, 6.3 and 7.5 ppm are observed. Figure 3.3b evidences the formation of the pyrrole ring at 5.6 ppm, the presence of CH\(_2\) unit attached to the pyrrol group in the OH moiety at 3.8
ppm, the protons associated to the benzene ring at 6.6 and 6.9 ppm, and the protons of OH groups at 9.2 ppm.

Figure 3

![Figure 3](image.png)

**Figure 3.** 1H-NMR spectra of PK30 modified with different ratios between furane (Fu) and OH groups (aliphatic-OH a and aromatic-OH b) at a maximal 80% of conversion.

The area below each signal changes according to the number of protons that belong to each functional group whereas the intensity of the signal assigned to the pyrrole ring remains constant. This trend well agrees with the formation of the desired structure, although a quantitative estimation is affected by peak overlapping. Furthermore, spectral data obtained by FT-IR analysis corroborate the 1H-NMR results. Figure 3.4A displays FT-IR spectra for PK30-Fu-Ap at two different conversion values. We start by noticing the appearance of broad peaks around 3400 cm\(^{-1}\) that belong to the OH group experiencing intermolecular hydrogen bonding, the pyrrole ring at 3115 and 1505 cm\(^{-1}\) and the furan moiety at 3150, 1145 and 738 cm\(^{-1}\).
Figure 3.4 FT-IR spectra of PK30 functionalized with furan / OH groups at different ratios, aliphatic OH (A) and aromatic OH (B). Figure C displays the magnification in the C-H bending region for B (furan peak 742 cm\(^{-1}\) and benzene peak 827 cm\(^{-1}\)). Bands normalized at 2962 cm\(^{-1}\) (C-H stretch).

The same holds true for PK30-Fu-Ty (Figure 3.4B) with the expected appearance of absorptions related to the benzyl ring at 1613 and 828 cm\(^{-1}\). In both cases (Figures 3.4A and 3.4B the intensity between the peaks of furan and OH groups change as a function of conversion. Figure 3.4C displays the magnification of the PK30-Fu-Ty spectra in the C-H
bending region for polymers bearing only furan or both furan and benzyl-OH groups at different conversion values. The figure clearly evidences the furan peak decreasing as conversion becomes in favour of benzyl-OH groups (i.e. out-of-plane C-H bending). All prepared polymers were characterized, before cross-linking, by DSC analysis (Figure 3.5).

**Figure 3.5** $T_g$ (measured by DSC) of PK30: as a function of different percentage of conversion with furfurylamine (PK30Fu), 3-amino-1-propanol (PK30Ap) and tyramine (PK30Ty) (A), as a function of different interacting side groups but same (~80%) total conversion and backbone structure (B) and as a function of different Fu / OH ratios at 80% total conversion (C).

Polymers with only one functional group (either Fu or OH) display a monotonous increase of $T_g$ with the amine conversion (Figure 3.5A). This is in agreement with the increased rigidity of the backbone by increasing the amount of pyrrole groups. Moreover, PK30 functionalized with aromatic OH groups (PK30-Ty) systematically displays (at equal conversion values) significantly higher $T_g$ than those modified with furane (PK30-Fu) and aliphatic OH groups (PK30-Ap). This behaviour is attributed to the bulkiness of tyramine (which increases the steric hindrance so that the energy demand to activate segmental motions) and the relevant
contribution (differences are up to 60 °C) provided by hydrogen bonding interactions. Also, PK30-Ty displays higher T_g values than PK30-Ap possibly due to the more acidic nature of phenyl-OH groups. This feature can be confirmed by the broad character of signals associated to hydrogen bonding of OH groups around 3420-3390 cm⁻¹ and considering the evident bathochromic shift (30 cm⁻¹ for PK30-Fu-Ty) by increasing the amount of tyramine moieties (Figure 3.4B). Moreover, taking into account the T_g values of PK30-Ba80 (14 °C) and PK30-Bea80 (42 °C), i.e. the polymers with no interacting side chains since modified by butylamine and benzylamine, respectively, the contribution of hydrogen bonding is evidenced (Figure 3.5B). As expected, samples of the PK30-Fu-OH series (thus displaying the presence of both hydrogen bonding and possibly aromatic interactions (e.g. PK30-Fu-Ty)) show T_g values intermediate between the ones of the two reference compounds (PK30-Fu80 and PK30-OH80) at the same total conversion value (Figure 3.5C). It is interesting to note in Figure 3.5C a deviation from linearity for PK30-Fu65-Ty15. This can possibly be ascribed to the total lower conversion of this system, compared to the others (see Table 3.1). It is worth noting that all DSC data clearly demonstrate, even before cross-linking, the remarkable versatility of the employed synthetic approach in yielding polymeric systems with tunable thermal behaviour as a function of composition.

On the other hand, it can also be speculated that T_g values may come from undesired cross-linking reactions occurring during the polymer modifications. In order to clarify this point, Gel Permeation Chromatography analysis was performed on the different products (Table 3.2). According to these results, it can be recognized that all systems display similar values of the polydispersity index (PDI) and practically the same magnitude of Mn and Mw, which proves that the different values obtained for T_g are only consequences of pyrrole formation, inter-polymeric interactions of functional groups and steric hindrance according to the bulkiness of each modifier as above mentioned.

The polymers were then cross-linked and de-cross-linked via a DA and r-DA sequence using an aromatic bis-maleimide (Figure 3.6). The cross-linking reactions of PK30-Fu and PK30-Fu-OH with bis-maleimide occurred at 50 °C for 24 h. All prepared samples were cross-linked with bis-maleimide in a ratio 1:1 between furane and maleimide groups. In a first step, DSC analysis was carried out in order to investigate the thermal behaviour of the prepared samples (Figure 3.7).
Figure 3.6 Schematic representation of DA / r-DA sequence and molding of functionalized polyketone PK-Fu-OH cross-linked with bis-maleimide. In red reversible covalent interactions and blue hydrogen bonding (aliphatic or aromatic).

In the heating and cooling runs, the occurrence of the Diels-Alder reaction (exothermic peaks) and its reverse process (endothermic peaks) are clearly visible. It is worth noting that each sample showed practically the same thermogram curves up to 3 cycles between 0 to 180 °C, thus confirming the full system reversibility. Moreover, the endothermic transition phase in all samples took place over a broad range of temperatures that reached values up to twenty degrees from the beginning to the end of the r-DA (i.e. the highest peak in the endothermic transition phase).

On the other hand, it is worth mentioning that the r-DA enthalpy (i.e. the area under the curve associated to the r-DA peak) is related to the energy required to break all DA adducts in each particular cross-linked system. According to this, one could assume in advance that the system containing the higher amount of furan/maleimide adducts (e.g. PK30-Fu80/Ma) should display the higher value of enthalpy when compared to those samples displaying the combination with Fu/b-Ma and hydrogen bonding OH groups. Indeed, the enthalpy value decreases (Figure 3.7A= 33.66 J/g > 3.7B= 11.18 J/g > 3.7C= 8.17 J/g) with decreasing amount of DA adducts. Notably, the almost quantitative overlap of the endothermic and exothermic traces clearly indicates the reversibility of the systems upon thermal treatment at least in terms of amount of DA adducts broken and formed, respectively.
The thermo-mechanical behaviour of all prepared samples (as solid bars) was tested by DMTA at four heating cycles. DMTA results demonstrated that the corresponding softening point (taken as peak of tan (δ) in the corresponding DMTA curves) increases with the amount of furan/maleimide adducts in systems bearing only Fu groups. This is expected on the basis of the corresponding network density (Figure 3.8).
Figure 3.8 Softening points (tan δ) tested by DMTA of PK30-Fu at different grade of conversions and PK30-Fu-OH systems at different ratios of functional groups cross-linked with bis-maleimide. Ratio Fu/Maleimide 1:1.

In systems containing both Fu and OH functional groups (*i.e.* at the same 80% of carbonyl conversion along the backbone), the corresponding softening point decreases with the relative amount of OH groups (*i.e.* hydrogen bonding interactions) with respect to the furan ones (*i.e.* DA adduct). The trend is not linear with composition (or at least it does not seem to follow a linear pattern) since hydrogen bonding between OH groups and the carbonyl ones on the bis-maleimide compound might also take place and thus decrease the amount of available OH groups. In addition, the recovery of mechanical properties (modulus in this case) seems to be fully quantitative for both PK30-Fu (Figure 3.9A) and PK30-Fu-OH (Figure 3.9B and 3.9C; for brevity only three samples are shown).
Figure 3.9 Dynamic thermo-mechanical behaviour of cross-linked PK30-Fu80 (A), PK30-Fu20-Ap60 (B), PK30-Fu35-Ty45 (C). $E'$: storage modulus, $E''$: loss modulus and $\Tan \delta$: softening point (dumping factor). Ratio Fu / Maleimide = 1.

Despite the relatively high softening point and the fully quantitative recovery of modulus during the thermal cycles and recycling (grained samples), the formation of reversible cross-
linking through DA reversible adducts seems to be a better option for the creation of materials with higher damping capabilities. However, the combination with hydrogen bonding discloses very interesting and promising pathways towards the design of tuneable (in terms of thermal properties) reversible thermosets. Actually, considerable compensation on the lack of DA cross-links is observed since no detrimental values of modulus are observed by the presence of hydrogen bonds. In fact, by comparing the three different systems in Figure 3.9, it is possibly to see that the elastic and loss modulus are increased by the contribution of hydrogen bonding. It is worth mentioning that the ratio $E'' / E' = \tan \delta$ (right axes in Figure 3.9) reach values of $3.9A = 0.15 < 3.9C = 0.28 < 3.9B = 0.32$ indicating the formation of more elastic materials by decreasing the Diels-Alder crosslink density, respectively.

In these particular systems (PK-Fu-OH), the addition of OH groups is crucially from two different points of view:

- from a scientific perspective it allows comparing polymers with the same backbone structure (vide supra), which in turn allows pinpointing the exact influence of hydrogen bonding on the thermal and mechanical behaviour;
- from an applicative point of view, it provides an easy and straightforward way to modulate the softening point of the final product while decreasing the chance of side reactions due to the fact that the carbonyl conversion is factually close to its theoretical maximum of 80% [38]. Moreover, the presence of OH groups increases the internal motion (friction) and relaxation of the polymeric chains during the applied stress. This certainly increases the intrinsic self-healing properties of the materials. It can be noticed by the fact that elastic and loss modulus remains practically as the original in continuous DMTA measurements (Figure 3.9) due to the faster recovery of the hydrogen bonds.

### 3.4 Conclusions

This work illustrates the facile synthesis of intrinsic thermally self-healing polymeric material based on the chemical modification of aliphatic polyketones by Paal-Knorr reaction. The modification of the polymers was proved to be feasible using conventional oil bath and microwaves heating to achieve similar end-products. Besides the easiness of the modification procedure, which constitutes a relevant novelty in the open literature, the Paal–Knorr reaction
with aliphatic and aromatic amine compounds provides a series of general advantages. In particular, it allows the preparation of a series of compounds displaying the same backbone structure but a (systematic) variation in the amount of hydrogen bonding and Diels-Alder active groups. From a scientific perspective this allows to pinpoint exactly the influence of both kinds of interactions on the thermal and mechanical behaviour. DSC traces indicated that furan / OH-functionalized polyketones are capable to be repeatedly cross-linked and de-cross-linked with bis-maleimide by only using heat as external stimulus. Furthermore, DMTA measurements testify the relevant contribution of Diels-Alder covalent bonding to the final softening point temperature while hydrogen bonding interactions seem to contribute to a faster and quantitative recovery of modulus in these systems.

3.5 References

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4 Thermally reversible rubber-toughened thermoset networks via Diels-Alder chemistry

**Abstract.** In this work we present a reversible and toughened thermoset system based on the covalent incorporation of a furan-functionalized ethylene-propylene rubber (EPM-Fu) into a thermoset furan-functionalized polyketone (PK-Fu) via Diels-Alder (DA) reversible cross-linking with bis-maleimide (b-MA). FT-IR and DSC analyses proved the reversible interaction between PK-Fu and EPM-Fu with b-Ma via DA and r-DA sequence. Likewise, thermo-mechanical experiments (DMTA) indicated the reworkability of the material with no evident differences in elastic and loss modulus after several heating cycles and recycling steps. Moreover, a considerable increase in the softening point (tan δ) was also found for the toughened system containing 12 wt. % of EPM-Fu (137 °C for the original thermoset and 155 °C for the toughened one). A two-fold increase in Izod impact strength compared to the original thermoset (up to 27 J/m) was also recorded for the toughened system. Overall, this approach clearly indicates that fully thermally reversible and toughened thermosets can be realized starting from mixtures of furan-functionalized polyketone and EPM rubber, cross-linked via reversible Diels-Alder chemistry.

**Keywords:** rubber toughening, reversible thermoset, Diels-Alder reaction, recycling.
4.1 Introduction

Thermosetting resins are polymers that upon heat or light radiation convert into insoluble polymer networks being cross-linked by covalent chemical bonds. Due to this network, thermosets offer many superior properties compared to thermoplastics such as mechanical strength, dimensional stability at elevated temperature and solvent resistance [1]. These features confer them the ability to be widely used as composites, adhesives and coatings. Unlike thermoplastics, thermoset cannot be re-melted or re-shaped, since they degrade or decompose upon heating. These features limit their recyclability [2] so that at the end of their service life, they are simply grinded to produce cheap reinforcement fillers or are thermally processed (pyrolysis, incineration) to recover the fiber content or just energy [3-5]. A more sustainable strategy for recycling is to re-design thermosets by replacing classical chemical cross-links with reversible covalent bonds [2] that can be repeatedly broken and re-connected by heating. These thermoreversible networks combine many mechanical properties of thermosets with the processability of thermoplastics [6], but with the added value of intrinsic self-healing properties [7]. Among several reversible reactions, the Diels-Alder (DA) [4π+2π] cycloaddition between furan and maleimide moieties is one of the most exploited in thermoreversible cross-linking [8]. First, DA is an equilibrium reaction influenced by temperature: covalent furan/maleimide adducts are formed at about 50 °C (cross-linking) and broken (de-cross-linking via retro DA) at about 120 °C. Furthermore, the cross-linking – de-cross-linking process can be repeated many times with negligible degradation [9] in the range of 50 °C – 150 °C. Finally, the strong dienic character of the furan ring and the high reactivity of the maleimide as a dienophile, ensure fast kinetics and high yields [10]. Most of the studied thermoreversible networks are based on DA reaction of polymers bearing pendant furan and/or maleimide groups, but their syntheses are often too expensive or complex to permit an industrial scale up. In contrast, a system based on aliphatic polyketones with pending furan groups and cross-linked with 1,1’-(methylenedi-4,1-phenylene)bis-maleimide was proposed as a promising low cost and efficient alternative [11]. Alternating aliphatic polyketones, obtained by copolymerization of carbon monoxide, ethylene and propylene were modified through the Paal-Knorr reaction to introduce furan groups directly attached to the backbone chain. The modification reaction proceeds in bulk with high yields and fast kinetics, producing water as only by-product. The thermoset obtained upon cross-linking with bis-maleimide was re-healed up to seven times, displaying quantitatively retained mechanical
properties [11]. Furthermore, thermal and mechanical properties could be modulated as a function of the degree of furan functionalization and the furan/maleimide molar ratio [12].

Besides the poor recyclability of thermosets currently on the market, they generally show a high brittleness compared to thermoplastics, due to their inadequacy in dissipating energy under mechanical stress. This causes poor resistance to crack formations as well as low fracture toughness and impact strength [1]. This point constitutes a major drawback in the application of thermosets, so that many systems were developed aimed at enhancing toughness in epoxy resins, being these materials widely used for structural applications. Those systems are essentially based on the incorporation of either rigid or soft toughening agents in the epoxy matrix as a separate phase [13]. These modifiers can be inorganic fillers as silica, glass beads [14, 15], engineered thermoplastics as polyphenylene oxide [16, 17], rubbery core-shell particles [18-20] or liquid reactive rubbers such as carboxyl-terminated (CTBN) and amine-terminated butadiene-acrylonitrile copolymers (ATBN) [21-23]. CTBN and ATBN are the most investigated and widely used on commercial scale since they improve toughness of the epoxy matrix without significantly affecting its bulk properties such modulus or $T_g$ [1]. As a common procedure, the liquid rubber is initially miscible with the uncured epoxy resin, while during the curing stage it irreversibly reacts with the epoxy through the functional groups (e.g. carboxylic or amino) and, as the molecular weight increases, it results in the formation of a second phase [24].

Herein we report an innovative procedure aimed at introducing rubber toughening to the polyketone/bis-maleimide system mentioned above, without interfering in the reversible character of the thermoset polymer. The rubber, an EPM grafted with furan groups, was chosen as a second cross-linked toughening phase as it can be easily prepared from commercial maleated EPM and reversibly cross-linked with bis-maleimide, as recently reported [25]. The furan-modified polyketone and EPM were blended in solution, at different weight ratios, and cross-linked with a bis-maleimide. The corresponding morphologies were investigated by means of electronic and optical microscopy whereas polymer toughness was determined in terms of Izod impact strength. Thermal reversibility was tested by FT-IR and DSC measurements while thermomechanical properties, reworkability and recyclability were evaluated by DMTA analysis.
4.2 Experimental section

Reagents

The alternating aliphatic polyketone (PK30, MW 2687 Da) presents a total olefin content of 30% of ethylene and 70% of propylene [26, 27]. Maleated ethylene/propylene rubber (EPM-MA, 49 wt.% ethylene, 49 wt.% propylene, 2.1 wt.% maleic anhydride, $M_w = 50$ kg/mol, PDI = 2.0) was kindly provided by LANXESS elastomers and dried in a vacuum oven at 175 °C for one hour to convert hydrolyzed diacids into anhydrides. Furfurylamine (Sigma-Aldrich, ≥99%) was freshly distilled before use. Tetrahydrofuran (THF, Sigma-Aldrich, >99.9%), acetone (Sigma-Aldrich, >99.5%) and 1,1’-(methylene-4,1-phenylene)bis-maleimide (Sigma-Aldrich, >95%) were purchased and used as received. Deuterated dimethylsulfoxide (DMSO-d$_6$, Sigma Aldrich, ≥99 atom%) was used as solvent for $^1$H-NMR measurements.

Furan-derivatization of PK30 via Paal-Knorr reaction

The reaction between PK30 and furfurylamine was carried out in bulk according to the Paal-Knorr reaction (Figure 4.1).

![Figure 4.1](image-url) Modification of the aliphatic polyketone in bulk via Paal-Knorr reaction.

In a typical experiment, about 60 g of PK30 were weighed into a sealed 250 ml round bottom glass reactor equipped with a U-type anchor impeller, a reflux condenser and an oil bath for heating. The reactor was heated to 110 °C and 35.4 g (0.365 mol) of furfurylamine, based on the targeted carbonyl conversion of 80% (i.e. the di-carbonyl unit of polyketone modified into pyrrole ring, Figure 4.1), were added dropwise during the first 20 minutes. The reaction was allowed to proceed for 4 hours. The light brown product (PK-Fu) was cooled with liquid
nitrogen, crushed and ground into small particles. The particles were washed three times with Milli-Q water to remove the unreacted furfurylamine, if any, filtered and freeze-dried for 24h.

The carbonyl conversion \( C_{CO} \) of PK was calculated according as follows:

\[
C_{CO} = \frac{y}{x+y} \cdot 100
\]

being \( x \) the moles of dicarbonyl unit and \( y \) the moles of pyrrolic unit (Figure 4.1) after conversion. \( y \) was calculated according to the formula:

\[
y = \frac{N}{M_N}
\]

where \( N \) is the weight in grams of nitrogen in the final product, as determined by elemental analysis and \( M_N \) is the atomic mass of nitrogen. \( x \) was calculated as follows:

\[
x = \frac{C \cdot M_C - y \cdot n_Y^C}{n_X^C}
\]

where \( C \) is the weight (grams) of carbon in the final product as determined by elemental analysis, \( M_C \) is the atomic mass of carbon, \( n_Y^C \) and \( n_X^C \) are the average number of carbons in the pyrrolic and in the dicarbonyl unit, respectively. Conversion efficiency \( (\eta) \) was calculated as follows:

\[
\eta = \frac{y}{mol_{Fa}} \cdot 100
\]

with \( mol_{Fa} \) being the moles of furfurylamine in the feed.

**Furan-derivatization of EPM-MA**

Typically 100.0 g of EPM-MA (21.42 mmol MA) were dissolved in 900 g THF by stirring for 24 h at room temperature in a closed flask. 6.24 g of furfurylamine (3 equivalents based on the molar content of maleic anhydride) were added to the solution and agitation was maintained for 12 h. After reaction, the product (EPM-Fu) was purified by mixing the polymer with 5 liters of acetone under mechanical stirring. Once the polymer precipitates as yellowish flakes, it is collected and dried in an oven at 50 °C up to constant weight. Conversion \( (C) \) of MA groups was calculated from FT-IR spectra according to a reported method [25], by using the following formula:
\[ C = \left(1 - \frac{A_{1856}^{Fu}}{A_{1856}^{Fu}A_{1856}^{MA}} \right) \cdot 100 \]  

(5)

where: \( A_{1856}^{Fu} \) and \( A_{1856}^{MA} \) are the integrals of the absorption bands at 1856 cm\(^{-1}\) (C=O asymmetric stretching of anhydride rings) for EPM-Fu and EPM-MA respectively; \( A_{723}^{Fu} \) and \( A_{723}^{MA} \) are the integrals of the bands at 723 cm\(^{-1}\) (methyl rocking), used as internal reference.

**Samples preparation and cross-linking**

PK-Fu and EPM-Fu (set at different weight ratios) were dissolved in a nine-fold amount of THF, in a round bottom flask equipped with a magnetic stirrer, an oil bath and a reflux condenser. The mixture was heated at 50 °C for 24 h. A stoichiometric amount of 1,1’-(methylenedi-4,1-phenylene)bis-maleimide (considering a 1:1 molar ratio between maleimide and the total amount of furan groups) was added to the mixture and the reaction (Diels-Alder cycloaddition) was allowed to proceed for 24 h under agitation at 50 °C. After reaction, the cross-linked gels were placed in a vacuum oven during 24 h at 50 °C to evaporate the solvent. Reference samples, one containing PK-Fu and EPM-MA (80:20 wt. % ratio) and another containing only PK-Fu, were prepared and cross-linked with bis-maleimide using the same procedure. An overview of all prepared systems is reported in Table 4.1. Samples have been coded by stating the type of EPM rubber and the percentage weight ratio rubber/polyketone.

**Table 4.1** Amounts of polyketone (PK-Fu), EPM rubber (EPM-Fu or EPM-MA) and 1,1’-(methylenedi-4,1-phenylene)bis-maleimide used to prepare the samples and resulting wt. % of rubber in each system.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PK-Fu (g)</th>
<th>EPM (g)</th>
<th>PK-Fu/EPM (w/w)</th>
<th>bis-maleimide (g)</th>
<th>Rubber (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK-Fu*</td>
<td>6.00</td>
<td>-</td>
<td>100:0</td>
<td>4.77 (13.3 mmol)</td>
<td>\text{-}</td>
</tr>
<tr>
<td>PK-Fu/EPM-Fu_10</td>
<td>5.41</td>
<td>0.60</td>
<td>90:10</td>
<td>4.31 (12.0 mmol)</td>
<td>6</td>
</tr>
<tr>
<td>PK-Fu/EPM-Fu_15</td>
<td>5.09</td>
<td>0.90</td>
<td>85:15</td>
<td>4.09 (11.4 mmol)</td>
<td>9</td>
</tr>
<tr>
<td>PK-Fu/EPM-Fu_20</td>
<td>4.80</td>
<td>1.20</td>
<td>80:20</td>
<td>3.86 (10.8 mmol)</td>
<td>12</td>
</tr>
<tr>
<td>PK-Fu/EPM-MA_20*</td>
<td>4.81</td>
<td>1.20</td>
<td>80:20</td>
<td>3.81 (10.6 mmol)</td>
<td>12</td>
</tr>
</tbody>
</table>

*Reference systems*
Characterization

Elemental analysis was performed with an EuroVector EA apparatus. $^1$H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using DMSO-$d_6$ as solvent. FT-IR spectra were obtained using a Perkin-Elmer Spectrum 2000. KBr pellets with 1.5 wt. % content of polymer were prepared from powders of the polyketone/rubber samples. Films (1 mm thick) were prepared from the EPM rubbers by compression molding at 180 °C for 30 minutes under a pressure of 100 bar. DSC thermograms were recorded on a TA-Instrument DSC 2920 under N$_2$ atmosphere. Samples were first heated from 0 °C to 180 °C and then cooled to 0 °C. Four cycles were performed at a rate of 10 °C per minute. Dynamic Mechanical Thermal Analysis (DMTA) was performed using a Rheometric scientific solid analyzer (RSA II) under air environment, in dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C per minute. Three cycles were performed for each sample, between room and softening temperature. DMTA specimens were 6 mm wide, 1.4 mm thick and 54 mm long. They were prepared by molding the cross-linked samples at 150 °C for 30 minutes under a pressure of 40 bar and then annealed in an oven at 50 °C for 24 hours. Izod impact strength was measured at room temperature, according to ASTM D4812 using standard unnotched specimens (12.7 mm wide, 3.3 mm thick and 64 mm long) prepared by compression molding of about 3.5 g of material in the same conditions used for DMTA specimens. Tests were performed on a Zwick 5102 Pendulum Impact Tester equipped with a hammer. At least 6 specimens for each sample were tested. Impact strength was calculated as the ratio between the energy absorbed in the impact and the thickness of the specimen. The morphological study of the systems was performed using a Philips XL30 Field-Emission Environmental Scanning Electron Microscopy SEM-FEG on fresh-fractured surfaces coated with gold nanoparticles (10 nm size). A simple observation on fracture toughness was registered using an optical microscope on samples prepared with the polymerography technique [28, 29].

4.3 Results and discussion

Synthesis of furan-functionalized polyketone

Furan-functionalized polyketone (PK-Fu) was synthesized by reacting PK30 with furfurylamine in bulk at 110 °C for 4 h (Figure 4.1). A high quantitative carbonyl conversion of 76% (80% targeted) and a conversion efficiency of 96% were obtained, confirming the
Paal-Knorr reaction as a simple and efficient route to modify polyketones, as previously reported [11, 12, 30]. $^1$H-NMR spectra of PK30 and PK-Fu are shown in Figure 4.2.

![Chemical structure](image)

**Figure 4.2** $^1$H-NMR spectra of unmodified polyketone (PK30, black curve) and furan modified polyketone (PK-Fu, red curve).

The resonance signals at 7.5, 6.3 and 6.1 ppm were assigned to protons on the furan ring connected to the polymer backbone, the resonance peak at 5.6 ppm was assigned to the protons of the pyrrole ring whereas the peak at 4.9 ppm was ascribed to the CH$_2$ group connecting the furan and the pyrrole ring [11, 12].

**Synthesis of furan-functionalized EPM rubber**

A pre-thermal treatment was performed on the EPM-MA rubber in vacuum at 175 °C in order to turn the hydrolyzed diacids moieties into maleic anhydrides [25, 31]. Subsequently, furan-functionalized EPM rubber (EPM-Fu) was synthesized by reacting EPM-MA and furfurylamine in a THF solution at room temperature. The resulting EPM-Fu rubber was then studied by FT-IR transmission (Figure 4.3). The appearance of the C-O-C symmetric stretching band at 1013 cm$^{-1}$ clearly proved the presence of furan groups in the product [32]. Furthermore, the shift of the band at 1856 cm$^{-1}$ to 1780 cm$^{-1}$ (C=O asymmetric stretching)
and the one from 1780 cm\(^{-1}\) to 1710 cm\(^{-1}\) (C=O stretching) in addition to the appearance of a new band at 1378 cm\(^{-1}\) (C-N symmetric stretching) demonstrated the conversion of anhydride rings into imide derivatives [12, 31, 33].

![Diagram of chemical reaction](image)

**Figure 4.3** FT-IR spectra of EPM-MA and the modified EPM-Fu: the reaction sequence is displayed in the inset.

A deconvolution analysis was used to integrate the areas related to the peaks at 1856 cm\(^{-1}\) (C=O asymmetric stretching) and 723 cm\(^{-1}\) (methyl rocking vibration). From their ratio, the reaction conversion was determined and was found to be >99.9%, thus demonstrating that the chemical modification process is quantitative.

**Cross-linking of polyketone/rubber blends via Diels-Alder cycloaddition**

PK-Fu/EPM-Fu blends were cross-linked with 1,1′-(methylene-4,1-phenylene)bis-maleimide in THF solutions at 50 °C for 24 h (see Table for experimental conditions). A scheme of one of the possible Diels-Alder (DA) adducts is reported in Figure 4.4. The FT-IR spectra of the sample PK-Fu/EPM-Fu_20 were recorded before and after the reaction with the bis-maleimide (Figure 4.5).
Figure 4.4 Cross-linking and de-cross-linking of furan-modified polyketone PK-Fu / EPM-Fu rubber blends via Diels Alder (DA) and retro-Diels-Alder (r-DA) sequence with 1,1’-(methylenedi-4,1-phenylene)bis-maleimide.

Figure 4.5 clearly displays the appearance of the band at 1185 cm$^{-1}$ (C-N-C stretching in succinimide ring of DA adduct) and the disappearing of the bands at 740 cm$^{-1}$ (out-of-plane proton bending) and 1011 cm$^{-1}$ ($V_s$ C-O-C) of unreacted furans. Notably, this result substantially proves the formation of Diels-Alder adducts [11, 12, 34, 35] while the band at 1378 cm$^{-1}$ (C-N stretching in maleimide rings) demonstrates the presence of the bis-maleimide.

Figure 4.5 FT-IR spectra of PK-Fu/EPM-Fu (80/20 wt. % ratio) blend before and after cross-linking with 1,1’-(methylenedi-4,1-phenylene)bis-maleimide.
All cross-linked samples were characterized by Differential Scanning Calorimetry (DSC) in order to determine the thermal history, reversibility and the exo / endo-thermal process related to the DA and r-DA sequence, respectively. All thermograms displayed a broad endothermic transition in the range of temperature 120-150 °C for each consecutive thermal cycle (Figure 4.6). The similarity in each consecutive thermal cycle demonstrates the reversible character of the cross-linked PK-Fu, even when blended with the rubber.

The endothermic transition corresponds to the r-DA process. Therefore, the peak of the curves corresponds to the temperature at which the majority of the DA adducts are broken (T_rDA_peak). The area under the curve associated to this peak, is therefore related to the energy absorbed during the cleavage of the DA adducts [7, 12]. Remarkably, it can be noticed that the energy absorbed during the r-DA process (Table 4.2) decreases as the rubber content increases in the systems. This trend can be explained considering that EPM-Fu has a lower moles number of furan groups per gram than the PK-Fu, thus less DA adducts are present in the blends compared to the neat cross-linked polyketone. Indeed, the lowest value in the

Figure 4.6 DSC thermal cycles of cross-linked PK-Fu/EPM-Fu_20. Only one sample was reported for clarity.
integral was obtained from the sample PK-Fu/EPM-MA_20, which contains the maleated EPM rubber. All systems containing the rubber displayed practically the same T_rDA peak and about eight degrees higher than the reference system PK-Fu. This can be possibly explained by the absorption of energy from the rubber during the process of r-DA and disentanglement [36, 37].

**Table 4.2** Calculated endothermic integral values (Area_{rDA}) and r-DA endothermic peak T_{rDA} in the 1st thermal cycle of PK-Fu, PK-Fu/EPM-Fu and PK-Fu/EPM-MA cross-linked with bis-maleimide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area_{rDA} (J/g)</th>
<th>T_{rDA} peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK-Fu*</td>
<td>19.74</td>
<td>141.8</td>
</tr>
<tr>
<td>PK-Fu/EPM-Fu_10</td>
<td>17.33</td>
<td>149.6</td>
</tr>
<tr>
<td>PK-Fu/EPM-Fu_15</td>
<td>16.68</td>
<td>149.7</td>
</tr>
<tr>
<td>PK-Fu/EPM-Fu_20</td>
<td>15.38</td>
<td>150.4</td>
</tr>
<tr>
<td>PK-Fu/EPM-MA_20*</td>
<td>13.31</td>
<td>150.4</td>
</tr>
</tbody>
</table>

*Reference samples

Homogeneous test-specimens for Dynamic-mechanical Thermal Analysis (DMTA) were successfully obtained from all samples, using hot compression molding. The variations in storage modulus (E’) and softening point (tan δ) as a function of the temperature and different amounts of rubber are shown in Figure 4.7.

For all samples the storage modulus (E’) exhibited a plateau followed by a sharp drop starting around 110 °C, implying a rubbery transition, but still cross-linked, due to a progressive softening of the entire system that probably loses some of the DA adducts during the process [8]. E’ values in the plateau region were in the same order of magnitude for all the systems, but a lower value (1.5 GPa) was observed for the sample with the highest content of rubber (PK-Fu/EPM-Fu_20), thus suggesting a less stiff material. The softening temperature, as determined from the peak of tan δ curves, was found within a narrow range (140-146 °C) for PK-Fu, PK-Fu/EPM-Fu_10, PK-Fu/EPM-Fu_15 and PK-Fu/EPM-MA_20, while significantly higher (155 °C) for PK-Fu/EPM-Fu_20.
After reaching the softening temperature, each sample was cooled down to room temperature during the first 10 minutes inside the DMTA chamber and tested again up to 3 heating cycles (Figure 4.8).

Storage and loss moduli were quantitatively recovered in each cycle, providing further evidence of the reworkability of the systems. Notably, the softening temperature slightly shifted to higher values (+5 °C) for samples containing the rubber. This shift can be attributed to a change from the kinetically endo to the thermodynamically more stable exo conformation of DA adducts after heating cycles [38].
Figure 4.8 Dynamic Mechanical Thermal Analysis of cross-linked samples PK-Fu (A), PK-Fu/EPMFu_10 (B) and PK-Fu/EPM-Fu_20 (C) in three consecutive cycles.
Figure 4.8 also shows that the presence of increasing amounts of rubber amplifies the system ability to recover loss modulus between cycles. According to this, the presence of rubber increases the system dimensional stability so that modulus remains practically as the original in continuous DMTA measurements when the concentration of rubber reached 12% (PK-Fu/EPM-Fu_20). After thermo-mechanical tests, all samples were re-grinded and reshaped by compression molding for further DMTA tests, in order to further check their recyclability (Figure 4.9).

**Figure 4.9** DMTA of cross-linked samples PK-Fu (A) and PK-Fu/EPM-Fu_20 (B): comparison between virgin (freshly molded, in black) and recycled (grinded and remolded, in green) material. The recycled samples were reshaped at 150 °C and 40 bar for 30 minutes.
It is worth noticing that both recycled samples displayed quantitative recovery of modulus and softening points. However, a slightly increase in softening point was observed for the neat PK-Fu thermoset sample, possibly due to a more effective endo to exo conformational change of the DA adducts (Figure 4.9). The relatively high softening point and the fully quantitative recovery of modulus and tan δ during thermo-mechanical cycles and recycling (grained samples), denotes that fully thermally reversible systems are possible to be made by the combination of furan functionalized polyketone with furan functionalized EPM rubber.

Izod Impact test was performed on unnotched specimens that broke completely during testing (Figure 4.10).

![Izod impact strength of all polymer samples](image)

**Figure 4.10** Izod impact strength of all polymer samples

All toughened samples display a monotonous increase in the impact strength with increased rubber content. For the sample PK-Fu/EPM-Fu_20 (12 wt. % of furan-modified rubber) a twofold increase was observed compared to the neat cross-linked polyketone. Moreover, a slightly higher value of impact strength for PK-Fu/EPM-Fu_20 compared to the reference PK-Fu/EPM-MA (12 wt. % of maleated rubber) was observed. This small difference can probably indicate that both EPM rubbers provide similar toughening effect on the cross-linked polyketone. However, the DA chemical interaction between the matrix and the furan-
functionalized rubber may be also taken into consideration. In order to clarify this point, a morphological study was performed by means of scanning electron microscopy (SEM) on fresh fractured surfaces in both toughened systems (Figure 4.11). The holes observed in the micrographs are cavitated spaces of detached rubber particles after the samples are broken. It is clearly noticed that EPM-MA and EPM-Fu rubber particles are embedded heterogeneously in size and morphology inside the matrix (Figure 4.11A and 4.11B). However, EPM-MA rubber particles leave smoother surfaces inside and around holes when removed, therefore suggesting poor compatibility and no chemical bonds between the two phases (Figure 4.11C). Differently, EPM-Fu rubber particles leave rough surfaces inside and around holes suggesting a well intrinsic adhesion between the phases. This fact might be explained by the interfacial chemical bond via DA active groups (Figure 4.11D).

![SEM micrographs of freshly broken surfaces of PK-Fu/EPM-MA_20 (A and C) and PK-Fu/EPM-Fu_20 (B and D) showing cavitated particles (indicated by white arrows) with different size and morphology.](image)

**Figure 4.11** SEM micrographs of freshly broken surfaces of PK-Fu/EPM-MA_20 (A and C) and PK-Fu/EPM-Fu_20 (B and D) showing cavitated particles (indicated by white arrows) with different size and morphology.
Figure 4.12 displays the toughening effect of EPM-MA and EPM-Fu rubber particles in the thermoset matrix after samples break. In Figure 4.12B, a crack that apparently propagates from right to left (black arrow) is deflected and bridged by EPM-MA rubber particles (red arrow). Moreover, some rubber particles are pulled-out or separated from the matrix as the crack propagates through the matrix. This can be explained by the weaker interaction between both phases as observed in Figure 4.11C and suggested by impact test results. On the other hand, Figures 4.12C and 4.12D show that crack propagation is stopped by EPM-Fu rubber particles. Deflection is also observed (black arrow, Figure 4.12D) but crack separation seems to be absent. Overall, this demonstrates the effective intrinsic adhesion between the phases possibly due to the presence of DA inter-linkers between them.

Figure 4.12 Optical micrographs of PK-Fu (A) PK-Fu/EPM-MA_20 (B) and PK-Fu/EPM-Fu_20 (C, D) at different magnifications displaying the toughening effect of rubber particles. Letter R indicates rubber particles.
4.4 Conclusions

We have demonstrated the facile synthesis of a reversible thermoset material based on the chemical modification of aliphatic polyketones with furfurylamine by the Paal-Knorr reaction. The cross-linking and the rubber toughening with functionalized furan-EPM rubber occur via Diels-Alder chemistry. Moreover, all the reaction involving polymers functionalization occur without adding any catalyst and in a conventional apparatus thus suggesting scaling up feasibility. Additionally, this approach successfully demonstrated thermo-mechanical, impact strength and recycling improvements on the neat thermoset. The combination of DSC and DMTA experiments effectively indicates that furan functionalized polyketones in combination with furan-functionalized rubber are capable to be repeatedly cross-linked and de-cross-linked with bis-maleimide by only using heat as external stimulus. Impact strength and morphological studies clearly demonstrated that the introduction of covalently bonded EPM rubber via Diels-Alder chemistry effectively improved the final impact strength of the toughened thermoset systems.

4.5 References

5 Exfoliation and stabilization of MWCNTs in a thermoplastic pyrrole-containing matrix assisted by hydrogen bonds

Abstract. This work focuses on the design of an engineered thermoplastic polymer containing pyrrole units in the main chain and hydroxyl pendant groups (A-PPy-OH), which help in achieving nanocomposites containing well-distributed, exfoliated and undamaged multi-walled carbon nanotubes (MWCNTs). The thermal annealing at 100 °C of the pristine nanocomposite promotes the redistribution of the nanotubes in terms of a percolative network, thus converting the insulating material in a conducting soft matrix (60 μΩ.m). This network remains unaltered after cooling to r.t. and to successive heating cycles up to 100 °C thanks to the effective stabilization of MWCNTs provided by the functional polymer matrix. Notably, the resistivity–temperature profile is very reproducible and with a negative temperature coefficient of -0.002 K⁻¹, which suggests the potential application of the composite as a temperature sensor.

Keywords: thermoplastic pyrrole-containing polymer, MWCNTs exfoliation, MWCNTs thermodynamic stabilization, hydrogen bonding, temperature sensor.
5.1 Introduction

Carbon nanotubes (CNTs) are one of the most popular fillers currently used in polymer nanocomposites (PNCs) [1]. CNTs are cylindrical forms of graphitic sheets displaying a single wall (SWCNT) or multi walls (MWCNT) with open or closed ends [2]. CNTs are inherently multifunctional so they can work as structural support [3], conductive [4, 5] and sensing platform in PNCs [6]. Conductive nanocomposites have been currently used in several commercial products [7]. Among them, PNCs with temperature sensing properties have become very attractive products in the open market due to their possibility of nanoscale tailoring and very low cost of production. Typically, these kinds of materials have shown a resistivity strictly dependent on temperature [8], thus opening successful applications in the field of miniaturized and potentially low cost plastic sensors [6, 9-12]. In some cases, the resistance variation proceeds by the dynamic interconnection/disconnection of the CNT network in the matrix [13]. However, temperature sensing properties of CNTs/polymer composites are demonstrated to be more reproducible when the resistive response is governed by the semi-conducting features of exfoliated and stabilized CNT networks under thermal solicitations [11].

Despite all advantages of electronic temperature-sensing PNCs over conventional thermometers, these kinds of materials are not exempt of problems. A common drawback in the design of resistive sensors based on CNTs/polymer composites is the strong tendency of CNTs to aggregate in bundles during composite processing due to the strong van der Waals interactions between their graphitic surfaces, which make their large-scale utilization problematic [7, 14, 15].

Several strategies to improve CNT dispersion in polymeric matrices have been reported in the open literature (e.g. CNT/in-situ polymerization composites, high-shear melts processing, injection molding etc. [16]). Among them, particularly attractive is the functionalization of the CNTs surfaces by the covalent attachment of functional groups [3, 16-18], but disruption of their sp² conducting network even occurs [19, 20]. A non-disruptive strategy used to disperse CNTs by means of conductive polypyrroles has been reported for applications in electronics [21, 22]. In these particular systems, the pyrrole groups get in contact with the sp² network of the CNTs surface via supramolecular π-π interactions, which promote the polymer wrapping around the filler. As a result, multilayers of the polymer form bridges that separate
CNTs from each other yielding effective percolation pathways. However, despite the good conductive properties, polypyrroles/MWCNTs composites are highly brittle so that they must be doped with counter ions or coated on flexible polymer substrates to improve their mechanical performance (e.g. fracture toughness)[23, 24].

Herein we report on the design of a thermoplastic OH-functionalized alternating aliphatic polypyrrole (A-PPy-OH) matrix, which is capable to exfoliate and stabilize MWCNTs without the need of surface modification of the filler. The thermoplastic polymer is designed by the chemical modification of alternating aliphatic polyketone PK via Paal-Knorr reaction with amine compounds. The production of the polymer [25] and its chemical modification [26] occurs in high yield, low cost and fast kinetic using relatively mild conditions in bulk and with water as the only by-product. Specifically, the reaction between the polymer and an OH-amine compound turns the alternating carbonyl backbone of PK into pyrrole units bearing hydroxyl moieties (Figure 5.1). The combination of the polymer with MWCNTs produces a malleable and conductive rubber-like nanocomposite displaying electronic temperature-sensing properties. On one hand, the pyrrolic backbone exfoliates and stabilizes bundles of MWCNTs via supramolecular π-π interactions with the graphitic surface of the filler during thermal annealing. On the other hand, the OH-functional groups pending from the pyrrole units assist the polymer during the thermal stress by hydrogen bonding interactions to keep its dimensional stability and mechanical features. In order to figure out the role of the OH-motifs, a reference polymer displaying the same pyrrolic backbone of A-PPy-OH was prepared by the chemical modification of PK with n-butylamine, where the hydroxyl group is replaced by a CH₃ group (A-PPy-CH₃). The CNTs exfoliation and their effective dispersion within polymer matrices were investigated by in-situ resistance measurements and charge-contrast SEM imaging, whereas composites resilience under thermal stress was investigated by DSC analysis. The electrical resistance of composites was eventually evaluated under thermal cycles between r.t. and 100 °C, to explore their potential for the development of sensitive, stable, and reproducible temperature sensors.
5.2 Experimental section

Reagents

The alternating aliphatic polyketone (PK30, MW 2687 Da, Mul et al. 2002 [27]) presents a total olefin content of 30% of ethylene and 70% of propylene. 3-amino-1-propanol (OH) (Acros), butylamine (CH₃) (Sigma Aldrich, 99%), 2,5-hexanedione (Sigma Aldrich 98%), multi-walled carbon nanotubes MWCNTs (O.D. 6-9 nm, L. 5 µm, Sigma-Aldrich 95% carbon), DMSO-D₆ (Laboratory-Scan, 99.5%), 1-methyl-2-pyrrolidinone (Sigma-Aldrich, 99.5%) were purchased and used as received.

Model reaction

A model reaction between stoichiometric amounts of 2,5-hexanedione (8.7 mmol) and 3-amino-1-propanol was carried out in order to identify the presence of any side product after the Paal-Knorr reaction [26]. The reaction was performed in bulk, in a 100 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was heated up to 100 °C during 4 h.

Functionalization of polyketone with alcohol pendant groups

The solvent-free Paal-Knorr reaction [26] between PK and 3-amino-1-propanol was carried out using different molar ratios between the 1,4-di-carbonyl groups of polyketone and 3-amino-1-propanol (Table 5.1). A reference polymer that displays the same backbone
structure, but bearing a CH₃ instead of an OH group was also prepared using butylamine instead of 3-amino-1-propanol in the Paal-Knorr reaction, with the aim of evaluating the effect of hydrogen bonds on the thermal resilience of the composite. These chemical modifications of the polyketone were carried out in a 250 mL round-bottom glass reactor equipped with a reflux condenser, a U-type anchor impeller and an oil bath for heating. First, 60 g of PK (0.455 moles of di-carbonyl unit) were preheated to a liquid state at 100 °C. Then, 3-amino-1-propanol or butylamine was added dropwise to the reactor during 20 min. Next, the stirring speed was set to 600 rpm and the reaction was carried out for 4 h. Initially, the reaction mixture was colourless, but gradually turned to brown due to pyrrole formation on the polymer backbone [26, 28, 29]. The resulting mixture was diluted with chloroform and washed 3 times with a 0.2 M NaCl Milli-Q water solution, to remove the unreacted 3-amino-1-propanol, if any. Thereafter, the organic phase was evaporated under vacuum at 50 °C for 24 h. Light-brown powders were obtained as final products. In order to avoid hydration, the samples were sealed in brown glass vials and stored at 6 °C for further characterization. The corresponding samples are coded as A-PPy-OHₐᵢ or A-PPy-CH₃ₐᵢ with aᵢ being the mol percentage of amine with respect to the carbonyl groups in the feed. The percentage of conversion of carbonyls (C_co) into pyrrole groups can be calculated as follows:

\[ C_{co} = \frac{y}{y+x} \cdot 100\% \]  

where x and y represent the moles of di-ketone and pyrrolic units after conversion, respectively (Figure 5.1). y can be calculated as follows:

\[ y = \frac{wt(N)}{A_m(N)} \]  

where wt(N) represents the grams of nitrogen in the final product according to elemental analysis, and A_m(N) is the atomic mass of nitrogen. x can be calculated as follows:

\[ x = \frac{g_{prod} \cdot y \cdot M_w^y}{M_w^{pk}} \]  

where g_{prod} represents the grams of product after conversion, \( M_w^y \) the molecular weight of the pyrrolic unit and \( M_w^{pk} \) the molecular weight of a 1,4 di-ketone unit (131.6 g/mol). The conversion efficiency \( \eta \) is defined as the ratio between the carbonyl conversion \( C_{co} \) and the targeted one according to the amount of polymer and amine compounds provided in the feed (\( C_{co}^{feed} \)).
\[ \eta = \frac{C_{co}}{C_{co}^{feed}} \cdot 100\% \quad (4) \]

the \( C_{co}^{feed} \) is calculated as follows:

\[ C_{co}^{feed} = \frac{Mol_{amine}}{Mol_{d-co}} \cdot 100\% \quad (5) \]

with \( Mol_{amine} \) representing the moles of amine compounds and \( Mol_{d-co} \) the moles of di-carbonyl units in the feed.

**Table 5.1** Chemical modification of PK with different amounts of 3-amino-1-propanol (OH) and butylamine (CH\(_3\)). Samples are coded by stating the target percentage of conversion of carbonyls into pyrrole units considering a maximal 80% (\( a_i \)) of modification [29].

<table>
<thead>
<tr>
<th>Sample</th>
<th>( Mol_{amine} ) (moles)</th>
<th>( C_{CO}^a ) (%)</th>
<th>( \eta^b ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PPy-OH20</td>
<td>0.091</td>
<td>15</td>
<td>75</td>
</tr>
<tr>
<td>A-PPy-OH40</td>
<td>0.182</td>
<td>36</td>
<td>90</td>
</tr>
<tr>
<td>A-PPy-OH60</td>
<td>0.274</td>
<td>57</td>
<td>95</td>
</tr>
<tr>
<td>A-PPy-OH80</td>
<td>0.365</td>
<td>79</td>
<td>99</td>
</tr>
<tr>
<td>A-PPy-CH(_3)80</td>
<td>0.365</td>
<td>78</td>
<td>98</td>
</tr>
</tbody>
</table>

\(^a\) \( C_{CO} \) is the \( \% \) of carbonyl conversion (determined by elemental analysis).

\(^b\) \( \eta \) is the conversion efficiency of carbonyl groups. In all samples 0.455 moles of di-carbonyl unit (60 g. of PK) were used.

**A-PPy-OH40 / MWCNTs composite**

A-PPy-OH40 and MWCNTs were mixed in N-methylpyrrolidone, a solvent reported as an effective dispersant for MWCNTs [17], using fixed amounts of polymer and different amounts of MWCNT expressed as wt.%. For this step, only one of the OH-functionalized polymers was selected aiming at the design of a flexible temperature-responsive nanocomposite [30] (Table 5.2).
Table 5.2 Experimental conditions of A-PPy-OH40 mixed with different wt.% of MWCNTs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer (g)</th>
<th>MWCNT (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PPy-OH40</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>A-PPy-OH40</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>A-PPy-OH40</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>A-PPy-OH40</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>A-PPy-OH40</td>
<td>4</td>
<td>10</td>
</tr>
</tbody>
</table>

In detail, 4 g of polymer were completely dissolved in N-methylpyrrolidone (10 vol.%). The required wt.% of MWCNTs was mixed with the same solvent and sonicated in a bath for 30 min and then poured to the polymer solution in a round bottomed flask at 50 °C for 24 h under stirring. Then, the mixture was rotary evaporated and finally transferred into a vacuum oven (80 °C for 72 h) to ensure the complete removal of the solvent.

**Characterization**

Elemental analysis was performed with an Euro EA elemental analyzer. It was used to establish the percentage of nitrogen in the modified polymers. $^1$H-NMR spectra were recorded on a Varian Mercury Plus 500 MHz apparatus using DMSO-d6 as solvent. ATR-FT-IR spectra were recorded using a Thermo Nicolet NEXUS 670 FT-IR. Differential scanning calorimetry DSC thermograms were recorded on a TA-Instrument DSC 2920 under N$_2$ atmosphere. The samples were weighed (10-17 mg) in an aluminium pan, which was then sealed. The samples were first heated from -20 to 180 °C and then cooled down to -20 °C. Four cycles were performed from -20 to 180 °C, with heating and cooling rates set to 10 °C/min. GPC measurements were performed with a HP1100 Hewlett-Packard instrument. The equipment consists of three 300 x 7.5 mm PLgel 3 μm MIXED-E columns in series and a GBC LC 1240 IR detector. The samples were dissolved in THF to obtain a final concentration of 1 mg/mL. THF was used as eluent at a flow rate of 1 mL/min at a temperature of 40 °C. The calibration was done using polystyrene as standard and the data were determined using PSS WinGPC software. Scanning electron microscope images were
acquired on a Philips XL30 Environmental SEM FEG instrument as previously reported [31, 32].

In-situ resistance measurements were performed during thermal annealing (at 100 °C) on samples (7.28 mm long, 5.85 mm wide, 1.25 mm thick) constrained between copper plates, connected to a multimeter and placed inside a chamber provided with a heater and a temperature controller (± 0.1 °C). Dynamic mechanical thermal analysis (DMTA) was conducted on a Rheometrics scientific solid analyzer (RSA II) under an air environment using the dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C/min between 0 and 35 °C. The samples for DMTA analysis were prepared by compression-molding of 500 mg of the composite into rectangular bars (6 mm wide, 1 mm thick, 54 mm long) at 150 °C for 30 min under a pressure of 40 bar to ensure full homogeneity.

5.3 Results and discussion

Model component preparation

Model compounds are useful to characterize the structure of complex polymer systems via effective and rapid investigation techniques such as 1H-NMR spectroscopy. Here, a model compound was prepared by reaction of 2,5-hexanedione (i.e. representative for the di-carbonyl moieties along the PK backbone) with 3-amino-1-propanol. This Paal-Knorr reaction resulted in the formation of a pyrrole unit, bearing a hydroxy terminated alkyl chain (Figure 5.2).

![Figure 5.2 1H-NMR spectrum of model compound prepared by reaction of 2,5-hexanedione with 3-amino-1-propanol. The signal of protons associated to the pyrrole ring is at 5.6 ppm, CH₂ units give signals at 1.6, 3.4 and 3.8 ppm and the -OH group gives a broad signal at 4.6 ppm.](image-url)
Paal-Knorr chemical modification of PK

The reactions between PKs and 3-amino-1-propanol (Figure 5.1) were carried out according to the different molar ratios as reported in Table 5.1. Notably, these functionalized PKs display a total carbonyl conversion ($C_{CO}$, measured by elemental analysis) close to the target conversion (relative efficiency, $\eta \geq 90\%$, see Table 5.1), with a slightly lower value for the A-PPy-OH20 sample only. This result validates the robustness and versatility of the Paal-Knorr reaction of PK. The formation of the desired modified PKs containing pyrrole units with –OH motifs was confirmed by $^1$H-NMR spectroscopy (A-PPy-OH40 sample, Figure 5.3).

![Figure 5.3 $^1$H-NMR spectrum of A-PPy-OH40 in DMSO-d$_6$.](image)

The $^1$H-NMR spectrum shows analogous signals to those found in the model compound (Figure 5.2), i.e. the pyrrole units at 5.8 ppm, the CH$_2$ in the pendant group attached to the pyrrole unit at 3.5 and 3.8 ppm, and the hydroxyl group at 4.65 ppm.

An increase in the ratio between the amine compound and the polyketone in the Paal-Knorr reaction leads to the expected higher degree of conversion of the carbonyl groups of polyketone backbone into pyrrole units, as shown by the increasing $C_{CO}$ values in the A-PPy-OH$_{ai}$ series from A-PPy-OH20 to A-PPy-OH80 (Table 5.1). The increase in the concentration of pyrrole units along the polymer backbone promotes polymer rigidity, as demonstrated by the enhancement in the $T_g$ values of the functionalized polymers (Figure 5.4).
Figure 5.4 $T_g$ of the polymers of the A-PPy-Oh$_a$ series (in black) and of A-PPy-CH$_3 80$ (in red), plotted as a function of the degree of carbonyl conversion ($C_{co}$). The $T_g$ values were measured by DSC in three temperature cycles from -20 to 180 °C.

The linear increase of the $T_g$ with $Cco$ is not only ascribed to the presence of pyrrole units in the backbone, but mainly to effective interactions between the -OH groups of the polymer chains. This hypothesis is suggested by the much higher $T_g$ value of A-PPy-Oh80 (58 °C) compared to that of A-PPy-CH$_3 80$ (14 °C), which is characterized by the same conversion degree but contains only a paraffinic moiety as pendant group. The role of -OH groups in promoting secondary interactions among macromolecules was further investigated by FT-IR spectroscopy (Figure 5.5).

Figure 5.5 FT-IR spectra of the A-PPy-Oh$_a$ series and A-PPy-CH$_3 a_i$. Numbers indicate final % of carbonyl conversion after Paal-Knorr reaction.
The characteristic band attributed to the -OH groups stretching modes (3600-3100 cm\(^{-1}\)) becomes progressively wider and shifts to lower energies as the degree of functionalization of the A-PPy-OHa\(a\)i polymers increases. This is likely due to the higher number of hydrogen donors (OH) in the polymer chains. According to the literature, hydrogen donors undergo highly directional interactions with their hydrogen acceptors [33, 34, 35]. In our case and according to Figure 5.5, the intensity of the peak varies according to the hydrogen bonding density, which depends on the degree of polymer modification. However, if a shift of the peak is observed, it might be attributed to the balance between different competing intermolecular hydrogen bonds [33]. So that, the red-shift of about 100 cm\(^{-1}\) observed in Figure 5.5 suggests that one single directional interaction of the -OH group can be excluded. This fact can be explained by the mobility of hydrogen bonding so that its interaction with different groups on the surface of the polymer could also take place as the conversion increases and the most probable hydrogen acceptor is decreased (i.e. carbonyl groups). Moreover, we cannot exclude at this stage that the broad band at about 3400 cm\(^{-1}\) could be also attributed to a slight but effective hydration of the sample. In any case, the contribution of the OH groups in getting higher \(T_g\) values compared to the paraffinic counterparts results crucial since GPC measurements of all polymer systems showed no significant differences between their molecular weights (Table 5.3).

<table>
<thead>
<tr>
<th>Experiments</th>
<th>(M_n) (x10(^3))</th>
<th>(M_w) (x10(^3))</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-PPy-OH20</td>
<td>3.2</td>
<td>7.6</td>
<td>2.4</td>
</tr>
<tr>
<td>A-PPy-OH40</td>
<td>3.0</td>
<td>7.0</td>
<td>2.3</td>
</tr>
<tr>
<td>A-PPy-OH60</td>
<td>2.9</td>
<td>6.7</td>
<td>2.3</td>
</tr>
<tr>
<td>A-PPy-OH80</td>
<td>2.7</td>
<td>6.2</td>
<td>2.3</td>
</tr>
<tr>
<td>A-PPy-CH(_3)80</td>
<td>3.4</td>
<td>6.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>
**A-PPy-OH40/MWCNTs composites**

Polymer nanocomposites were designed with the aim to target a flexible, light and temperature-responsive system. In this attempt, A-PPy-OH40 was chosen among the A-PPy-OHa polymers because its $T_g$ is close to room temperature, and this is expected to provide the desirable flexibility of the composite at easily accessible temperatures. Moreover, this feature supports the use of the A-PPy-OH40/MWCNTs system as a resistive sensor for temperature variations close to the physiological regime. The A-PPy-OH40/MWCNT composites were prepared by mixing A-PPy-OH40 with different amounts of MWCNTs (Table 5.2) in N-methylpyrrolidone. The presence of MWCNTs causes an increase in the $T_g$ of the composite materials compared to the parent polymer (Figure 5.6).

![Figure 5.6](image)

**Figure 5.6** $T_g$ of the composites obtained by mixing A-PPy-OH40 with different wt.% of MWCNTs. The $T_g$ values were measured by DSC in three temperature cycles from -20 to 180 °C.

According to the literature, the increase of $T_g$ values with MWCNTs loading in polymeric systems is found to be related to the increment in their viscosity [36, 37] due to the interfacial interaction between matrix and filler at molecular level. Functional aromatic groups included in the backbone or as pendant groups in polymer chains, get in contact with the graphitic surface of the filler via supramolecular $\pi-\pi$ interactions. This behaviour hinders the mobility of the polymer chains and hence increases the $T_g$ [38-40]. Conductive polypyrroles have been reported as good dispersant agents for CNTs due to the interfacial connection of the filler with the pyrrole groups via $\pi-\pi$ interactions. In our case, the backbone of the polymer
contains 36% of pyrrole units that possibly promote effective interactions with the graphitic structure of CNT. In order to determine MWCNTs exfoliation, the 4 wt.% MWCNT/A-PPy-OH40 nanocomposite was analysed by SEM (Figure 5.7).

![SEM image](image)

**Figure 5.7** SEM morphological study of 4 wt.% MWCNT / A-PPy-OH40 nanocomposite.

The SEM image clearly shows the single (unbundled) nanotubes as the dominant species, thus confirming the good interactions between MWCNTs and the A-PPy-OH40 matrix.

With the aim to further improve the dispersion of the MWCNTs in the polymer matrix in terms of a fibrous percolative structure, the rubber-like composite containing 4 wt.% of MWCNT was subjected to thermal annealing at a constant temperature of 100 °C for 3 h and then cooled down to r.t. During the annealing, in-situ resistivity on the compressed mold specimen were measured in order to evaluate the effect of the thermal treatment on the formation of the conductive MWCNTs network within the polymer matrix. Before annealing, the resistivity of the polymer was infinite but it decreased sharply to ≈ 60 µΩ·m during the first minutes of thermal annealing and well persisted after cooling (Figure 5.8).
Figure 5.8 In-situ electrical measurement of 4 wt.% MWCNT / A-PPy-OH40 composite during thermal annealing at 100 °C. In the inset, a magnification of the first annealing instants.

This behaviour indicates that the thermal treatment at 100 °C effectively reorganizes MWCNTs structures within the polymer bulk in a well-defined percolative network. These remarkable changes easily occurred upon a mild thermal treatment, which is however effective in promoting polymer matrix mobility.

A morphological study of the composite analyzed by SEM in contrast mode [32] corroborates the electrical measurements of the nanocomposite before and after annealing (Figure 5.9). The micrographs taken from the surface of freshly teared samples revealed that bundles of MWCNTs are still present in the A-PPy-OH40 before annealing as evidenced at high magnification (Figure 5.9B). Conversely, after annealing a fiber-like polymer/MWCNT network is observed (Figures 5.9C). This indicates that the thermal treatment at 100 °C favors MWCNTs debundling and promotes their homogeneous dispersion in the polymer matrix (Figure 5.9D) in a percolative network.
Figure 5.9 SEM morphological study of 4 wt.% MWCNT / A-PPy-OH40 composite before (A, B) and after thermal annealing (C, D) at 100 °C.

The thermal history of the 4 wt.% MWCNT / A-PPy-OH40 nanocomposite after thermal annealing was evaluated by DSC analysis in order to establish the resilience of the material under the investigated temperature regime (Figure 5.10).

Figure 5.10 Three consecutive DSC thermal cycles (indicated by the arrow) of 4 wt.% MWCNTs / A-PPy-OH40 composite after annealing.
The similarity in each consecutive thermal cycle demonstrates the resilient character of the material without any sign of thermal degradation until 180 °C. The thermal traces also indicate that the same thermodynamic response of the composite remains upon heating, thus indicating no phase separation between the components. Considering that the $T_g$ of the composite is around 40 °C, it is worth noting that the sample does not display any endothermic transition during the annealing at 100 °C. This is another prove of the role played by the $–$OH groups in keeping the dimension stability of the composite. Figure 5.11 shows a picture with two different materials after being subjected to dynamic mechanical thermal analysis (DMTA) (from r.t. to 35 °C).

**Figure 5.11** Pictures of two different nanocomposites displaying their differences in dimension stability (damping capability of the material) after being tested by dynamic mechanical thermal analysis DMTA (Data about modulus not showed for brevity).

A-PPy-OH40/MWCNT is capable to keep its dimensions. Contrarily, A-PPy-CH380/MWCNT gets completely deformed. This suggests that the presence of hydrogen bonding plays a relevant role in giving dimensional stability to the material. The resistivity response of the polymer/MWCNT nanocomposite towards consecutive temperature cycles was monitored between r.t. and 100 °C (Figure 5.12).

**Figure 5.12** In-situ electrical measurements of 4 wt.% MWCNT / A-PPy-OH40 composite during three consecutive thermal cycles between r.t. and 100 °C.
Reproducible resistance variations were observed, with maximum amplitudes of 51 to 59 µOhm·m within the temperature interval of 80 °C. Moreover, the resistivity–temperature profile was very reproducible and with a negative temperature, thus proving that the percolation network does not experience any significant changes during the heating-cooling cycles. The electrical response with temperature shows a negative temperature coefficient of resistance [41, 42] of -0.002 K⁻¹ (average of three temperature cycles), an absolute value that is comparable to the highest values found in metals (0.0037–0.006 K⁻¹, 0.00385 K⁻¹ for a Pt100 sensor) and similar to other CNT/polymer nanocomposites reported in the literature [6, 11, 13].

5.4 Conclusions

We have demonstrated that a thermoplastic pyrrole-containing matrix is an effective dispersant for MWCNTs exfoliation. The polymer was prepared via the Paal-Knorr modification of an alternating aliphatic polyketone (PK) with OH-amine compound. The chemical reaction turns the waxy PK into a flexible rubber-like OH-functionalized pyrrole-containing polymer with tuneable T_g depending on the amounts of -OH groups. The polymer is able to generate non-covalent functionalization of the MWCNT graphitic materials through effective π-π interactions, and that the exfoliation process does not do significant damage to the one-dimensional CNT structure. SEM micrographs and DSC traces demonstrate that the A-PPy-OH/MWCNTs nanocomposite is capable to undergo continuous thermal cycles from -20 to 180 °C without any sign of interphase modification and matrix degradation. Notably, the conductive CNT network is maintained after several temperature cycles (from r.t. to 100 °C) proving the remarkable stability of the MWCNT homogeneous dispersion within the polymer matrix. Measurements repeated over three successive heating cycles revealed highly reproducible resistivity variations with negative temperature coefficient of about -0.002 K⁻¹, an absolute value comparable to the values found in metals. Overall, this data consistently support the use of A-PPy-OH/MWCNT nanocomposite as a soft and highly reproducible resistive sensor for temperature variations.

5.5 References

Electrically-responsive thermoset nanocomposite based on Diels-Alder chemistry

Abstract. In this work, a nanocomposite-based thermoset material with thermally reversible cross-linkages was designed and prepared by cross-linking a furan-functionalized polyketone (PK-Fu) with bis-maleimide and reinforced with multi-walled carbon nanotubes (MWCNTs) via Diels-Alder (DA) reversible cycloaddition. The main novel property of this material is that self-healing can be induced by resistive heating. The incorporation of 5 wt.% of MWCNTs results in an increased modulus of the material and makes it thermally and electrically conductive. XPS analysis indicates that the MWCNTs, due to their diene/dienophile character, covalently interact with both furan and maleimide groups via Diels-Alder reaction, leading to good interfacial adhesion between filler and matrix. Moreover, the softening point (taken as tangent δ in DMTA measurements) increases to 155 °C upon the addition of MWCNTs, as compared to the value of 130 °C for the unreinforced thermoset. After thermo-mechanical strain is applied, the composite diminishes its mechanical strength since heating above 150 °C triggers the retro-DA process that disrupts the network. Nevertheless, the mechanical properties of the composite are completely recovered by reconnecting the decoupled DA linkages via electrical resistive heating.

Keywords: Self-healing, resistive heating, conductive thermoset nanocomposite, reworkability, reversible Diels-Alder cycloaddition.
6.1 Introduction

Thermoset polymers are an important class of materials used in a broad range of applications, including coatings, adhesives and electrical insulators [1]. Thermosets, unlike thermoplastics, are characterized by a curing reaction that transforms two liquid components, or a paste [2], into a solid network structure. Due to this network, thermosets offer many superior properties compared to thermoplastics, such as mechanical strength, dimensional stability at elevated temperature and solvent resistance. However, thermoset systems are still facing challenges related to thermal, chemical and photo-degradation and high brittleness. Typically, undetectable micro-cracks can appear under loading thus leading to macroscopic fractures at a relatively small strain [3-5]. To overcome this drawback, thermosets have been combined with different kinds of fillers such as silica and glass beads [6, 7], engineered thermoplastics as polyphenylene oxide [8, 9], rubbery core-shell particles [10-12], and carbon fibers [13, 14] in order to design suitable load-bearing materials for structural applications.

Intensive research efforts are currently dedicated to synthesize thermoset nanocomposites with the aim of improving strength, modulus, and toughness of polymer matrices [15-18]. As a common procedure, the weight content of the filler in the matrix is tailored in order to gain the maximal reinforcement from the filler considering its aspect ratio and loading. Accordingly, the inclusion of small amounts of filler (< 5 wt.%) is often used to improve the mechanical properties of the matrix. Contrarily, filler amounts exceeding the loading threshold possibly generate the failure of the whole system due to the loss of effective interactions between the components at the interface [19, 20]. In this respect, the chemical functionalization of nanofillers via covalent attachment of compatibilizing functional groups or polymers has been reported to increase the mechanical performance of the nanocomposites even using relatively high filler loading [20-22].

A promising strategy employed in the fabrication of long-lasting nanocomposite systems is the incorporation of healing mechanisms for damage repair [23, 24]. Among several approaches, self-mendable thermoset nanocomposites have been designed according to different procedures in order to create autonomous and non-autonomous self-repairing systems [25-28]. In the case of non-autonomous self-mendable systems (i.e. intrinsic self-healing [28, 29]), the matrix experiences healing damage thanks to the presence of active functional moieties, which are triggered by external stimuli like heat [30] or light [31]. The two most exploited thermal methods currently used for the healing process are based on
Diels-Alder (DA) chemistry (reversible covalent cycloaddition) and/or hydrogen bonding (reversible non-covalent interaction)[32-36].

Electrically-induced self-healing is a relatively new concept currently employed in the design of long-lasting nanocomposites for electronic applications and actuators [37-42]. For these particular systems, the healing process occurs via the nanoscopic heat generation when the electrical current passes through a conductive nanostructured network [43]. The so-called Joule-effect (or resistive heating) activates the intrinsic self-healing ability of thermally self-mendable matrices in order to heal damage on local areas. Among several advantages, this approach guarantees a faster healing process even at a nanoscale level, thus representing an extraordinary alternative for curing and self-healing in engineering thermoset applications that are impossible for conventional heating procedures [44, 45].

In previous works, alternating aliphatic polyketones (PK) obtained by the copolymerization of carbon monoxide, ethylene, and propylene were chemically modified by the Paal-Knorr reaction to introduce furan groups directly attached to the backbone chain. The chemical reaction proceeded in the bulk with high yields and relatively fast kinetics, producing water as the only by-product [46-48]. The grafted furan groups allowed the formation of three-dimensional polymer network structures after being cross-linked with aromatic bis-maleimide. The materials indeed formed thermally reversible and self-healing thermosets by means of DA and retro-DA (r-DA) sequence employing conventional heating procedures.

Herein we report on the intrinsic self-healing ability induced by resistive heating of an electrically conductive thermoset nanocomposite based on the chemical modification of an alternating aliphatic polyketone grafted with furan groups (PK-Fu) via Paal-Knorr reaction, cross-linked with bis-maleimide and reinforced with MWCNTs via reversible Diels-Alder cycloaddition. Spectroscopic investigations were used to assess the modification of the starting polyketone, the cross-linking of the resulting polymer, and the chemical bonding with the nanofiller via DA reaction. Thermo-mechanical tests allowed evaluating the mechanical performance and self-healing ability of the composite. Results concerning the material modulus were correlated with electrical measurements, spectroscopy and IR thermography. The morphology of the system was analysed by electronic microscopy before and after healing by resistive heating.
6.2 Experimental section

Reagents

The alternating aliphatic polyketone (PK30, MW 2687 Da) presents a total olefin content of 30% of ethylene and 70% of propylene [49]. Furfurylamine (Fu) (Aldrich, ≥ 99 %) was freshly distilled before used, and benzylamine (Bea) (Sigma Aldrich 99 %), multi-walled carbon nanotubes (MWCNTs) (O.D. 6-9 nm, average length 5 µm, Sigma-Aldrich 95 % carbon), DMSO-d6 (Laboratory-Scan, 99.5%), (1,1-(methylene-4,1-phenylene)bis-maleimide (b-Ma) (Sigma Aldrich 95 %), 1-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99.5 %), tetrahydrofuran (THF, Laboratory-Scan, 99.5 %), chloroform (CHCl3, Laboratory-Scan, 99.5 %) and deuterated chloroform (CDCl3, Sigma Aldrich 99.8 atom% D) were purchased and used as received.

Functionalization of Polyketone with furan and benzyl groups

The reaction between PK and furfurylamine was carried out in bulk by the Paal-Knorr reaction [50] and the molar ratio between the reactants (i.e. the di-carbonyl group of polyketone and the amine group of furfurylamine) was established as percentages with a maximal conversion of 80 % according to Zhang et al. 2009 and Toncelli et al. 2012 [47, 48]. In order to establish more clearly the role of the furan motifs, a polymer grafted with benzyl groups was prepared by the Paal-Knorr reaction and used as a reference. This so-called PK-Bea displays the same backbone structure of PK-Fu but non-reactive pendant groups, at least in our conditions, by Diels-Alder cycloaddition (Figure 6.1, see Paal-Knorr experimental procedures in previous chapters).

![Figure 6.1 Schematic representation of PK functionalized with furan (PK-Fu) or benzyl (PK-Bea) groups via Paal-Knorr reaction.](image-url)
PK-Fu Cross-linked with b-Ma via Diels-Alder reaction

The DA reaction of PK-Fu (10 g) with bis-maleimide was carried out at a furan / maleimide molar ratio of 1:1 using THF as solvent (≈ 10 wt.% polymer based on solvent) in a 250 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The reaction mixture was heated up to 50 °C for 24 h to form the polymer network. After reaction, the cross-linked polymer was dried at 50 °C under vacuum overnight to remove the solvent.

Functionalization of MWCNTs with PK-Fu or b-Ma via Diels-Alder reaction

PK-Fu (0.95 g) was dissolved in 5 mL of NMP and added to 0.05 g of MWCNT (previously sonicated for 30 min in 5 mL of NMP). The reaction was set under vigorous stirring at 50 °C for 24 h using an oil bath equipped with a temperature controller. The reaction mixture was repeatedly washed with THF, filtered and the remaining solvent removed under vacuum at 50 °C for 48 h. The same procedure was used to mix MWCNTs with bis-maleimide. A sample containing MWCNTs and PK30-Bea was used as a reference since no chemical interaction is expected between the components. The percentage of grafted product (\(\text{grafted} \ (%)\)) can be calculated as follows:

\[
\text{grafted} \ (%) = \frac{\text{Prod}_{\text{recov}}}{\text{Graf}_{\text{prod}}} \cdot 100
\]  

(1)

where \(\text{Prod}_{\text{recov}}\) represents the amount of material recovered after filtering the excess of compound that did not react with MWCNTs; \(\text{Graf}_{\text{prod}}\) represents the amount of PK-Fu, PK-Bea or b-Ma (in grams) grafted on the MWCNTs surface. The \(\text{Graf}_{\text{prod}}\) is calculated as follows:

\[
\text{Graf}_{\text{prod}} = M_w \cdot \text{moles} \ (N)
\]  

(2)

where \(M_w\) represents the molecular weight of the functionalized pyrrolic unit of PK-Fu and PK-Bea (in the case of b-Ma, the two nitrogens of the molecule are considered) and \(\text{moles} \ (N)\) are the moles of the pyrrolic unit or maleimide groups according to the moles of nitrogen obtained by elemental analysis (see Figure 6.1). The moles of nitrogen are calculated as follows:

\[
\text{moles} \ (N) = \frac{g^{(N)}}{A_m^{(N)}}
\]  

(3)
where \( g(N) \) represents the grams of nitrogen according to elemental analysis and \( A_m(N) \) the atomic mass of nitrogen. Finally, the \( g(N) \) can be calculated as follows:

\[
g(N) = \text{Prod}_{\text{recoy}} \cdot N_{\text{content}}
\]

where \( N_{\text{content}} \) represents the percentage of nitrogen estimated by elemental analysis.

**PK-Fu / b-Ma / MWCNTs composite**

The thermoset nanocomposite was prepared by one-pot solvent-mix containing equimolar amounts of PK-Fu and b-Ma (at a furan / maleimide ratio of 1:1) and 5 wt.% of MWCNTs. The reactants were previously dissolved in THF (\( \approx 10 \) wt.\%) and bath sonicated for 30 min in a 150 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was heated up to 50 °C for 24 h to form the cross-linked network under reflux. After reaction, the solvent was removed under vacuum at 50 °C overnight. The resulting powder was divided into small pieces of nearly 500 mg that were molded into rectangular bars at 150 °C for 30 min under a pressure of 40 bar. A neat thermoset sample without MWCNTs was also prepared for comparison. After molding, the samples were cooled down to room temperature (30 minutes) and then stored at -17 °C for further analysis.

**Characterization**

The elemental composition of the samples was analyzed using an Euro EA elemental analyzer. \(^1\)H-NMR spectra were recorded on a Varian Mercury Plus 400 MHz apparatus using deuterated chloroform as solvent. FT-IR spectra were collected using a Perkin-Elmer Spectrum 2000. The sample pellets were prepared by mixing potassium bromide (KBr) with the polymer (\( \approx 1.5 \) wt.%). The powder was then kept under vacuum at 50 °C for 24 h to remove residual water. ATR-FTIR spectra were recorded using a Thermo Nicolet NEXUS 670 FT-IR. Differential Scanning Calorimetry (DSC) analysis was performed on a TA-Instrument DSC 2920 under \( \text{N}_2 \) atmosphere. The samples were weighed (10-17 mg) in an aluminum pan, which was then sealed. Hereafter, the samples were heated from 0 to 180 °C and then cooled to 0 °C. Four heating-cooling cycles were performed at a rate of 10 °C/min. GPC measurements were performed with a HP1100 Hewlett-Packard. The equipment consists of three 300 x 7.5 mm PLgel 3 \( \mu \)m MIXED-E columns in series and a GBC LC 1240 IR detector. The samples were dissolved in THF (1 mg/mL) and eluted at a flow rate of 1 mL/min at a temperature of 40 °C. The calibration curve was made using polystyrene as
standard and the data were interpolated using the PSS WinGPC software. Thermogravimetric analyses (TGA) were carried out in a nitrogen environment on a PerkinElmer TGA 7 instrument from 20 °C to 700 °C at a heating rate of 10 °C/min. Dynamic Mechanical Thermal Analyses (DMTA) were conducted on a rheometrics scientific solid analyzer (RSA II) under air environment using the dual cantilever mode at an oscillation frequency of 1 Hz and a heating rate of 3 °C/min. The samples for DMTA analysis were prepared by compression molding of 500 mg of the composite into rectangular bars (6 mm wide, 1 mm thick, 54 mm long) at 150 °C for 30 min under a pressure of 40 bar to ensure full homogeneity. Electrical measurements were performed on the rectangular bars used for DMTA analysis. The setup consisted of a power supply (EA-PS 3150-04 B) and a multimeter (FLUKE 175). Electrical parameters were measured on samples connected to a conventional circuit using copper clamps holders. The surface resistivity ($\rho_s$) was calculated as follows:

$$\rho_s = \frac{V}{L} \div \frac{I}{W}$$

where $V$ is the voltage supplied in the electrical circuit, $L$ is the distance in meters between the electrodes connected to the sample, $I$ is the current measured in amperes and $W$ is the width of the sample in meters. Thermal images were obtained using a FLUKE IR thermometer camera (VT02) from samples subjected to electrical current. X-ray photoelectron spectroscopy (XPS) was carried out with a SSX-100 (Surface Science Instruments) spectrometer equipped with a monochromatic Al Ka X-ray source ($h\nu = 1486.6$ eV) that operates at a base pressure of $3 \times 10^{-10}$ mbar. The energy resolution was set at 1.45 eV, the photoelectron take-off angle was 37° with respect to the surface normal and the diameter of the analyzed spot was 600 μm. Spectra were collected at a minimum of two different spots on each sample, checked for consistency and averaged for each spectral interval. The data were fitted using the Winspec software [51] applying the Shirley background and a linear combination of Gaussian and Lorentzian peaks (mixing ratio of 0.8). All samples were re-suspended in toluene and deposited dropwise on Au substrates. After the solvent was evaporated, the samples were transferred into ultra-high vacuum via a load-lock system. Samples containing the pure polymer display broadened peaks due to sample charging effects. Therefore, the fitting width was set at 2.1 eV. The binding energy scale was corrected by using the C=C $sp^2$ signal at 284.4 eV as a reference [52]. Scanning electron microscope micrographs were taken with a Philips XL30S Environmental SEM-FEG instrument. High resolution images were acquired on freshly broken surfaces.
6.3 Results and discussion

PK functionalized with furan and benzyl groups via Paal-Knorr reaction

The solvent-free Paal-Knorr reaction between PK and the amine compounds was carried out using different molar ratios between the 1,4-di-carbonyl groups of polyketone and furfurylamine or benzylamine aiming at a maximal conversion of 80%. The summary of the experimental results is displayed in Table 1.

Table 6.1 Experimental results of PK modified with furfurylamine (PK-Fu) and benzylamine (PK-Bea).

<table>
<thead>
<tr>
<th>Run</th>
<th>(\text{C}_{\text{CO}}) (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>(\eta) (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>(T_g) (°C)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PK-Fu</td>
<td>74</td>
<td>92</td>
<td>31</td>
<td>2.3</td>
</tr>
<tr>
<td>PK-Bea</td>
<td>73</td>
<td>91</td>
<td>42</td>
<td>2.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Carbonyl conversion, <sup>b</sup> conversion efficiency. <sup>c</sup> glass transition temperature. <sup>d</sup> polydispersity index.

Notably, functionalized polyketones display a carbonyl conversion (\(\text{C}_{\text{CO}}\), measured by elemental analysis) close to the target conversion (efficiency, \(\eta > 90\%\), see Table 6.1). This result validates the robustness and versatility of the Paal-Knorr reaction with polyketones. For brevity, only the spectral characterization of PK-Fu is displayed in Figure 6.2. Figure 6.2A shows the \(^1\text{H}-\text{NMR}\) spectrum of the polymer mixed with furfurylamine before and after the chemical reaction. After modification, the characteristic peaks of the pyrrole appear in the spectrum, namely the proton signal ascribed to \(\text{CH}_2\) groups between the pyrrole and the furan groups at 4.9 ppm, the one related to the pyrrole group at 5.8 ppm and proton signals of the furan moieties at 5.9, 6.2 and 7.3 ppm [46, 47]. The FT-IR spectrum of the same sample is displayed in Figure 6.2B. It is possible to notice the appearance of C-H stretching related to the heterocyclic groups around 3150-3115 cm\(^{-1}\) (pyrrole and furan groups), the C=O stretching of the residual carbonyl groups at 1707 cm\(^{-1}\), the C=C stretching of the heterocyclic groups at 1507 cm\(^{-1}\), the pyrrole C-N stretching at 1345 cm\(^{-1}\), the furan C-O-C stretching at 1073 cm\(^{-1}\) and eventually the out-of-plane bending of the furan ring C-H bonds at 735 cm\(^{-1}\).
The $T_g$ of the functionalized polymers was measured by DSC (Table 6.1). As expected, the chemical modification of the di-carbonyl arrangement into pyrrole groups increases the rigidity of the backbone. Indeed PK30-Fu and PK30-Bea show a $T_g$ of 31 °C and 42 °C, respectively, *i.e.* much higher than that of PK before modification (-12 °C). GPC measurements showed no significant differences in the PDI of the two systems, indicating the absence of significant irreversible side reactions. The comparison of the two systems suggests that benzyl pendant groups confer stronger supramolecular interaction among the macromolecular chains with respect to that provided by furan moieties. This highlights the versatility of the PK system, whose modification with different amino compounds grafted on the same backbone allows tuning the $T_g$ value of the ultimate polymer.
Functionalization of MWCNTs with PK-Fu or b-Ma via Diels-Alder reaction

Figure 6.3 displays schematically the reaction between MWCNTs and PK-Fu or b-Ma. The amount of PK-Fu and b-Ma attached to the MWCNTs surface was evaluated by elemental analysis and TGA (Table 6.2).

**Figure 6.3** Functionalization of MWCNTs with A) PK-Fu (diene) and B) bis-maleimide (dienophile) via Diels-Alder reaction.

**Table 6.2** Experimental results for the functionalization of MWCNTs with PK-Fu, PK-Bea and bis-maleimide.

<table>
<thead>
<tr>
<th>Run</th>
<th>N content (%)</th>
<th>Grafted (%)(^a)</th>
<th>Grafted (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/PK30-Fu80</td>
<td>2.45</td>
<td>34</td>
<td>27</td>
</tr>
<tr>
<td>MWCNT/PK30-Bea80</td>
<td>0.83</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>MWCNT/b-Ma</td>
<td>0.62</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

*Grafted compounds (%) on the surface of MWCNTs are estimated by \(^a\) elemental analysis (nitrogen (N) content) and \(^b\) TGA.*

The results obtained by EA clearly establish the presence of nitrogen in the final samples. Conversely, no presence of nitrogen was found in un-functionalized MWCNTs within the detection limit of the apparatus (0.01 wt.%). The values of nitrogen obtained for the grafted MWCNTs/PK-Fu suggest that considerably higher functionalization of the filler is obtained as compared to MWCNTs/b-Ma. This is quite logic as PK-Fu contains many nitrogen atoms.
along the chain. In the case of MWCNTs mixed with PK-Bea, no covalent interaction is expected, thus the result obtained by EA might only suggest that effective physical mixing between the polymer and the filler occurs via π-π staking interactions [53-55]. Thermogravimetric analyses were also performed to establish the amount of PK-Fu and bis-maleimide covalently attached to MWCNTs (Table 6.2 and Figure 6.4). TGA results show clear differences between the un-functionalized and the functionalized MWCNTs. However, lower values of grafting are obtained from TGA results, as compared to EA, which might be explained by the fact that at 700 °C no degradation of the grafted materials is detected (see the slope at the final temperature of degradation in Figure 6.4). The temperature of degradation for the functionalized MWCNTs systems starts around 100 °C due to the presence of residual water. The larger weight loss of MWCNT-PK-Fu clearly indicates the successful attachment of the polymer on the surface of the MWCNTs. Moreover, the weight loss fraction of the grafted compounds follows the same trend as compared with the values of nitrogen calculated from EA (see Table 6.2).

![TGA analyses of pristine and functionalized MWCNTs with PK-Fu, b-Ma and the reference sample PK-Bea.](image)

**Figure 6.4** TGA analyses of pristine and functionalized MWCNTs with PK-Fu, b-Ma and the reference sample PK-Bea.

In literature, the formation of covalent bonds between cyclopentadiene, furan and bis-maleimide with CNTs via DA chemistry has been already proved by means of X-ray photoelectron spectroscopy [52, 56]. Herein, XPS analysis of the MWCNTs functionalized with PK-Fu clearly revealed the presence of nitrogen 1s and oxygen 1s signals (Figure 6.5).
It is worth noting that in the carbon 1s spectra, differences between the modified and unmodified MWCNTs surfaces can be identified; for the un-modified MWCNTs the main peak at 284.5 eV, accompanied by the shake-up feature at about 6.0 eV higher binding energy characteristic of $\pi$-$\pi$ conjugated systems, perfectly fits with C sp$^2$ reported in the literature [52, 56]. On the other hand, the C 1s spectrum of the pure polymer shows a broad feature peaked at 285 eV and resulting from three components: C-C sp$^2$, -CH$_2$ -CH$_3$ sp$^3$ and CH$_2$-C-CH$_3$, which are too closely spaced in binding energy [52] to be resolved in our experimental conditions. The spectrum for the pure polymer also shows O 1s components attributed to O=C at 532.4 eV and to O-C at 533.8 eV, as well as an N 1s peak at 401.5 eV; all these components perfectly agree with PK-Fu structure. For the product obtained after the grafting PK-Fu to the MWCNTs, the presence of the polymer is evident from the N 1s and O 1s intensities. In the C 1s spectrum, a broad peak was observed which was here fitted with a linear combination of the pure polymer and MWCNTs signal (respectively in dotted and dashed lines). While it is difficult to conclude from the C 1s spectrum that the sidewall functionalization of MWCNTs with PK-Fu proceeds via C-C bonding from the C 1s spectrum, in the O 1s spectrum the O-C component results shifted by 1 eV to higher binding energy, clearly pointing at a charge redistribution resulting from the furan attachment on the MWCNTs surface.

**PK-Fu / b-Ma / MWCNTs composite**

The thermoset nanocomposite was obtained in the form of highly homogeneous rectangular bars by one-pot solvent-mix containing equimolar amounts of PK-Fu and b-Ma (ratio 1:1
between Fu and Ma groups) and 5 wt.% of MWCNTs followed by compression-molding [46].

The neat thermoset (not shown for brevity) and the nanocomposite (Figure 6.6) were characterized by DSC to determine their thermal behavior, reversibility and the exo / endo-thermal processes related to the DA and retro-DA sequence, respectively. The thermograms display a broad endothermic transition in the range of temperature between 120 and 180 °C for each consecutive thermal cycle. The similarity between the three thermal cycles clearly indicates the reworkable character of the cross-linked PK-Fu even when reinforced with the MWCNTs. The endothermic transition corresponds to the r-DA process. Therefore, the peak of the curves corresponds to the average temperature at which the majority of the DA adducts are broken and the area under the curve associated to this peak is related to the energy absorbed during the cleavage of the DA adducts.

The DSC analysis of the nanocomposite evidences that the presence of MWCNTs has no apparent effect on the thermal behaviour of the thermoset [57]. Indeed, the energy associated to the r-DA process was calculated to be 11.1 J/g for the nanocomposite and 10.9 J/g for the neat thermoset, thus suggesting that the presence of the filler does not interfere with the r-DA process of the matrix [57]. In other words, even if a covalent interaction between matrix and filler occurs, the corresponding thermal transition is not visible in the DSC traces due to either overlap with the one associated to Fu-Ma or simply relatively low concentration.

![DSC thermal cycles of PK-Fu cross-linked with b-Ma and reinforced with MWCNTs.](image)

**Figure 6.6** DSC thermal cycles of PK-Fu cross-linked with b-Ma and reinforced with MWCNTs.
DMTA analysis performed on rectangular bars of materials shows that the filler leads to clear enhancements of softening point (peak Tan δ), loss and elastic moduli with respect to the neat thermoset system (Figure 6.7).

Figure 6.7 Dynamic Mechanical Thermal Analysis of PK-Fu cross-linked with b-Ma (filled squares) and PK-Fu cross-linked with b-Ma and reinforced with 5 wt. % of MWCNTs (empty squares).

In particular, the softening point (Tan δ) is increased from ~130 °C for the neat thermoset to ~155 °C for the composite. This can be explained by the fact that MWCNTs reinforce the inner-frame structure of the matrix that consequently increases its rigidity. This effect is aided by the interfacial interaction between the matrix and the filler via DA cycloaddition, as suggested by XPS analyses. As a result, the filler helps in dispersing the applied force and consequently improves the mechanical performance of the composite. Another phenomenon that possibly contributes in the softening point enhancement is the potential catalytic effect exerted by MWCNTs on the DA reaction between PK-Fu and b-Ma, which leads to higher cross-linking density [58].

The thermo-mechanical features of PK-Fu cross-linked with b-Ma and reinforced with MWCNTs were also determined after compression at 150 °C and 40 bar for 30 min. This process was supposed to favour r-DA mechanism and the consequent de-cross-linking of the thermoset nanocomposite. Figure 6.8 displays the thermo-mechanical behaviour of the de-cross-linked network and after healing by resistive heating at 35 V for 24h.
Figure 6.8 DMTA of PK-Fu cross-linked with b-Ma and reinforced with 5 wt.% of MWCNTs, after pressed at 150 °C and 40 bar for 30 min (filled squares) and after healing by passing a current through the sample during 24 h using 35 V.

It is worth noting that the elastic modulus (E’) and the softening temperature (Tan δ) are significantly improved after healing as compared with the system after molding. The electrical current applied as energy source effectively induces heat dissipation from MWCNTs, which triggers the reconnection between decoupled DA adducts thus re-establishes the cross-linked network [59]. A schematic representation of the proposed mechanism is reported in Figure 6.9.

Figure 6.9 Schematic representation of PK-Fu cross-linked with b-Ma and reinforced with MWCNTs. Arrows display the process of: 1) cross-linking (DA), 2) molding (partial r-DA) and 3) healing (DA) with resistive heating.
In order to confirm this idea, we monitored the temperature of the sample when a current goes through it (Figure 6.10).

![Figure 6.10](image)

**Figure 6.10** (A) Photograph of the PK-Fu/b-Ma/MWCNTs composite sample connected to the electrical circuit and its thermal images before (B) and during the application of a voltage of 35 V (C).

Notably, the well distributed red colour all along the film surface clearly suggests the homogeneous distribution of MWCNTs in the thermoset nanocomposite. The temperature reached by the network during the application of the electrical current corresponds to about 55-60 °C, *i.e.* a temperature at which DA processes between decoupled furan/maleimide moieties occur as demonstrated for thermal healing using a conventional oven [45, 47, 60].

The sequence of cross-linking in solution, de-cross-linking during molding and healing by resistive heating of the nanocomposite was also monitored by ATR-FTIR spectroscopy (Figure 6.11). The normalized spectra at 2930 cm\(^{-1}\) (C-H stretch, Figure 6.11A) and at 1145 cm\(^{-1}\) (C-N stretching band [61], Figure 6.11B) evidence the intensity variations of the C-N-C peak at 1185 cm\(^{-1}\) attributed to the stretching of the succinimide ring in the DA adduct). It is worth noting that the DA band decreased in intensity after molding (decoupling of DA adducts), whereas it promptly recovered after healing to intensities similarly collected form the nanocomposite thermally cross-linked in solution.
Figure 6.11 ATR-FTIR spectra of PK-Fu cross-linked with b-Ma and reinforced with MWCNTs. The different colors refer to the processes of: cross-linking (DA) (black), molding (partial rupture of DA adducts or r-DA) (red) and healing by resistive heating (reconnection of DA adducts) (blue).

According to the results displayed in Figure 6.11, part of the DA adducts are broken after molding, which could possibly favour re-agglomeration of MWCNTs. To support this hypothesis, resistive measurements and morphological studies by SEM were combined in order to figure out the degree of dispersion of MWCNTs in the matrix (Table 6.3, Figure 6.12).

Higher surface resistivity (about 228 Ω/cm²) was observed for the compressed bar after molding as compared with the one healed by 24 h of resistive heating (about 206 Ω/cm²). This result suggests the potentiality offered by the resistive heating in providing a better percolative network (Table 6.3) [62].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>After molding</th>
<th>After healing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (A)</td>
<td>30.7 ± 1.2</td>
<td>33.9 ± 0.3</td>
</tr>
<tr>
<td>ρs (Ω/cm²)</td>
<td>228.02 ± 9.5</td>
<td>206.3 ± 1.8</td>
</tr>
</tbody>
</table>
Contrast mode SEM micrographs [63] corroborate the results obtained from electrical measurements on the same sample after being molded and successively healed by resistive heating (Figure 6.12). On the freshly broken surfaces of the composite after molding (Figure 6.12A, 6.12C), bundles of MWCNTs (indicated by white arrows) can be observed. Conversely, a better distribution of MWCNTs is present after resistive heating (Figures 6.12B, 6.12D), thus confirming the ability of the electric current in restoring a more effective percolative network.

6.4 Conclusions

We designed an intrinsic self-healing thermoset/MWCNT nanocomposite capable to recover structural damage by means of thermally reversible Diels-Alder links activated by resistive heating. The thermoset matrix demonstrated to chemically interact with the filler due to the diene/dienophile character of MWCNTs. By this approach, it was possible to realize a
thermoset nanocomposite displaying a relatively high softening point (Tan δ) and electrical conductive properties. Thermo-mechanical measurements as well as spectroscopy and microscopy analysis clearly established the reworkability and intrinsic self-healing character of the thermoset nanocomposite via Diels-Alder chemistry using resistive heating as external stimulus. In addition, the industrial scale by which PK can be produced and chemically modified offers a straightforward alternative for the industrial production of electrically conductive thermoset nanocomposites displaying self-healing ability by resistive heating activation of reversible Diels-Alder adducts.

6.5 References

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51. LISE laboratory, Namur University, Belgium. Winspec software.


7 Appendix

7.1 Summary

Over the last few decades, researchers working on the design and optimization of plastic materials have reported considerable improvements (e.g. in mechanical properties of recycled materials) often stimulated by societal driven demands in terms of sustainability, enhancement of material quality and value-add services. However, despite all the efforts, it is widely recognized that plastic recycling is still facing relevant problems regarding collection, separation, cleaning, processing chemistry, and flow markets for recycled products. In the particular case of thermoplastics, suitable materials for recycling are subjected to the availability of treatment technology (e.g. re-melting, re-shaping) and markets. Unlike thermoplastics, thermosetting resins are polymers that upon heat or light radiation convert into infusible and insoluble polymer networks being cross-linked by covalent chemical bonds. Due to this network, thermosets offer many superior properties compared to thermoplastics such as mechanical strength, dimensional stability at elevated temperature and solvent resistance. These features confer them the ability to be widely used as composites, adhesives, and coatings. However, thermosets cannot be re-melted or re-shaped, since they degrade or decompose upon heating or by chemical treatments. These features limit their recyclability so that at the end of their service life, they are simply grinded to produce cheap reinforcement fillers or are thermally processed (pyrolysis, incineration) to recover the fiber content or just energy. A more sustainable strategy is to re-design thermosets by replacing classical chemical cross-links by reversible covalent bonds that can be repeatedly broken and re-connected by heating. These thermoreversible networks combine many mechanical properties of thermosets with the processability of thermoplastics. In addition, they can be designed to provide intrinsic self-healing properties.

In this thesis, chapters 2 and 3 focused on the chemical modification of alternating aliphatic polyketone with aliphatic and aromatic amine compounds using the Paal-Knorr reaction to obtain thermally reversible polymers with relatively high glass transition temperatures (i.e. a $T_g$ window from 100 °C to 185 °C). Both chapters highlight the tuneable thermal properties of polymers containing furan (Diels-Alder) and hydrogen bonding active groups directly attached to the backbone. The reversible thermosetting of furan-functionalized polymers via a Diels-Alder and retro-Diels-Alder sequence with bis-maleimide was investigated and
systematically compared with thermoset polymers containing both reversible covalent and supramolecular interactions.

Chapter 4 reports on the preparation of a reversible and toughened thermoset system based on the covalent incorporation of furan-functionalized ethylene-propylene rubber into a thermoset furan-functionalized polyketone. Spectroscopy and thermal analyses proved the reversible interaction between the functionalized polymers with b-Ma via DA and r-DA sequence. Likewise, thermo-mechanical experiments indicated the reworkability of the material with no evident differences in elastic and loss modulus after several heating cycles and recycling steps. Moreover, a considerable increase in the softening point (also known as damping factor) was also found for the toughened system containing the furan-functionalized rubber. A two-fold increase in Izod impact strength compared to the original thermoset was also recorded for the toughened system.

Chapter 5 focused on the design of an engineered thermoplastic polymer containing pyrrole units in the main chain and hydroxyl pendant groups, which help in achieving nanocomposites containing well-distributed, exfoliated and undamaged MWCNTs. The incorporation of MWCNTs made it possible to change the material from an insulator to a conductive system displaying temperature sensor properties. Notably, the resistivity-temperature profile is very reproducible which suggests the potential application of the composite as a temperature sensor.

Chapter 6 describes the electrically-induced self-healing properties of a thermoset nanocomposite designed by mixing furan-functionalized polyketone cross-linked with aromatic bis-maleimide and MWCNTs via Diels-Alder (DA) reversible cycloaddition. The incorporation of MWCNTs increases the material modulus and allowed electrical and thermal conduction. XPS analysis indicates that the MWCNTs, due to their diene/dienophile character, covalently interact with both furan and maleimide groups via Diels-Alder reaction, leading to good interfacial adhesion between filler and matrix. It is also demonstrated that above the thermal stability of the composite, the retro-DA process is triggered disrupting the network. Hence, the mechanical properties of the material are diminished due to the decoupling of DA adducts. Nevertheless, the mechanical properties are completely recovered after the sample is healed through electrical resistive heating.
7.2 Samenvatting

In de afgelopen decennia hebben onderzoekers die aan het ontwerp en de optimalisatie van kunststoffen werken aanzienlijke verbeteringen gerapporteerd (bijv. in de mechanische eigenschappen van gerecyclede materialen). Deze verbeteringen zijn vaak gestimuleerd door eisen vanuit de maatschappij op het gebied van duurzaamheid en verbetering van de kwaliteit van het materiaal. Echter, ondanks alle inspanningen is het is algemeen erkend dat plastic recycling nog steeds onderhevig is aan relevante problemen met betrekking tot inzameling, scheiding, schoonmaken, verwerken van de chemie en de markten voor de gerecyclede producten. In het specifieke geval van thermoplasten zijn geschikte materialen voor recycling onderhevig aan de beschikbaarheid van behandelingstechnologie (bijvoorbeeld hersmelten en hervormen) en markten. Anders dan bij thermoplasten worden thermohardende harsen na een behandeling met warmte of licht omgezet in onsmeltbare en onoplosbare polymere netwerken die met covalente chemische bindingen vernet zijn. Dit netwerk geeft thermoharders duidelijk betere eigenschappen vergeleken met thermoplasten. Dit heeft met name betrekking op de mechanische kracht, vormvastheid bij hoge temperatuur en bestendigheid tegen oplosmiddelen. Deze eigenschappen zorgen er voor dat ze op grote schaal worden gebruikt als composieten, hechtmiddelen en coatings. Thermoharders kunnen echter niet opnieuw worden gesmolten en opnieuw worden vormgegeven omdat ze degraderen of ontleden bij verwarming of door chemische behandelingen. Dit beperkt hun recycleerbaarheid en zorgt er voor dat ze einde van hun levensduur gewoon vermalen worden tot goedkope vulstoffen of thermisch behandeld worden (dmv pyrolyse of verbranding) om de vezels of ten minste wat energie terug te winnen. Een meer duurzame strategie is gevonden in het herontwerpen van thermoharders door de klassieke netwerkchemie te vervangen met door omkeerbare covalente bindingen die herhaaldelijk kunnen worden afgebroken en opnieuw met elkaar verbonden kunnen worden door ze te verwarmen. Deze thermo-reversibele netwerken combineren veel mechanische eigenschappen van thermoharders met de verwerkbaarheid van thermoplasten. Bovendien kunnen ze worden ontworpen om voor intrinsieke zelfherstellende eigenschappen van materialen te zorgen.

Hoofdstukken 2 en 3 van dit proefschrift zij gericht op de chemische modificatie van alternerende alifatische polyketon met alifatische en aromatische amineverbindingen via de Paal-Knorr reactie om thermisch reversibele polymeren met relatief hoge glasovergangstemperaturen (een $T_g$ venster van 100 °C tot 185 °C) te verkrijgen. Beide hoofdstukken
Hoofdstuk 4 beschrijft de bereiding van een reversibele en geharde vesterkte thermoharder die gebaseerd is op de covalente interactie tussen furan-gefunctionaliseerde etheen-propeen rubbers en een matrix van furan-gefunctionaliseerd polyketon. Spectroscopie en thermische analyse werden gebruikt om de reversibele interactie tussen de gefunctionaliseerde polymeren met bismaleimide via DA en de retro-DA reactie te laten zien. Eveneens werden thermomechanische experimenten gebruikt om de her-verwerkbaarheid van het materiaal zonder duidelijke verschillen in elastische en verliesmodulus na verschillende verwarmingsperioden en recycling stappen te demonstreren. Bovendien werd een aanzienlijke toename van de verwekingstemperatuur (ook bekend als dempingfactor) gevonden voor het systeem dat versterkt was met het furan-gefunctionaliseerde rubber. Een verdubbeling van de Izod slagsterkte ten opzichte van de oorspronkelijke thermoharder werd ook verkregen voor het met rubber versterkte systeem.

Hoofdstuk 5 is gericht op het ontwerp van een thermoplastische polymeer met pyrrool eenheden in de hoofdketen en hydroxyl zijgroepen die helpen bij het mengen van ontvouwen en onbeschadigde MWCNTs in nanocomposieten. De inmengen van MWCNTs maakte het mogelijk om het materiaal van een isolator in een geleidende systeem met temperatuursensor eigenschappen te veranderen. Met name het weerstand-temperatuur profiel is van deze materialen is zeer reproduceerbaar en nodigt uit om deze composiet in een toepassing als temperatuursensor te gebruiken.

Hoofdstuk 6 beschrijft de elektrisch geïnduceerde zelfherstellende eigenschappen van een thermohardest nanocomposiet dat gemaakt is door furan-gefunctionaliseerde polyketonen te vernetten met aromatische bis-maleïmides en MWCNTs via de reversibele Diels-Alder (DA) cycloadditie. De opname van MWCNTs verhoogt de modulus van het materiaal en zorgt voor elektrische en thermische geleiding. XPS-analyse laat zien dat de MWCNTs, vanwege hun dien/diënofiel karakter, een covalente interactie met zowel furan als maleïmidegroepen hebben via Diels-Alder-reactie. Hierdoor ontstaat er een goede grensvlak hechting tussen de
vulstof en de polymere matrix. Het is ook aangetoond dat een gegeven temperatuur, de retro-DA proces het netwerk verstoort. Zodoende worden de mechanische eigenschappen van het materiaal verminderd door het ontkoppelen van de DA adducten. Desalniettemin zijn de mechanische eigenschappen volledig hersteld nadat het monster is gerepareerd door middel van elektrische weerstandsverwarming.
7.3 List of publications


7.4 Contribution to international conferences


7.5 Acknowledgements

My biggest gratitude is to my parents, Mercedes and Valdemar, who have sacrificed their own life for my education and the education of my brother. My biggest thankfulness is to my wife for supporting me during more than eleven years and giving me the most beautiful thing that someone can give to you, another life! (my daughter Gabriela). I thank my brother Esteban for his support during all these years that we have been studying so far from home.

I would like to express my sincere gratitude to my supervisor Prof. dr. Francesco Picchioni for his continuous support during my PhD, for his motivation during bad times, and the immense knowledge transfer. His guidance helped me during all this time of research and writing of this thesis. Since the beginning of my PhD he showed himself not only as a supervisor, but also as a friend. Most of all, I thank him his reliance over my capacities. It was a risky bet: to trust in a marine biologist to finish a PhD in a chemical engineering environment.

I would like to thank the reading committee of my thesis: Prof. dr. Katja Loos, Prof. dr. H. J. (Erik) Heeres, and Prof. dr. Eduardo Soto for their insightful comments and encouragement to widen my research from various perspectives.

My sincere thanks also goes to Prof. dr. Andrea Pucci for his friendship and enormous transfer of knowledge during my research work and writing of scientific articles. Likewise, I would like to thank professors: dr. Paolo Pescarmona, dr. Petra Rudolf, dr. A. A. (Ton) Broekhuis, dr. Ignacio Moreno Villoslada and dr. Patrizio Raffa for their insightful comments and enlightening advices during my research work and writing of scientific articles.

My sincere thanks also goes to Marcel de Vries, Anne Appledoorn and Erwin Wilbers for all their help to resolve technical issues during my work in the laboratory. Likewise, I want to thank to Jan Henk Marsman and Léon Rohrbach for their help with the analytical measurements during all my PhD research. Also, I want to thank to Gert Alberda van Ekenstein for his insightful advices and help during thermal and mechanical characterization. I would like to thank Professor dr. Václav Ocelík for his insightful advices regarding microscopy characterization. My special thanks goes to Marya de Jonge who solved all my bureaucratic problems. Most of all, I appreciate her patience to teach me het ongeloofelijk moeilijk taal van Netherlands. I also thank Annette Korringa for her help regarding the arrangement of bureaucratic issues of my scholarship and university administrations.
All the work here presented could not be possible to conduct without the help of all my collaborators and colleagues. My sincere thanks goes to Guilherme Rooweder Lima, Giovanni Fortunato, Dian Santosa, dr. Mario Flores, dr. Parisa Pourhossein, Martijn Beljaars, Machiel van Essen, Mattia Lenti and Régis Gengler. My special thanks goes to my friends and colleagues dr. Patrizio Raffa, dr. Diego Wever, Lorenzo Polgar (many thanks for your help with all Dutch translations of my thesis), Graham Ramalho, Pablo Druetta, Patrick Figarooa, Arjen Kamphuis, Bilal Niazi, Eric Benjamins and Arne Hommes with who I could mix very funny moments and work at the same time.

My sincere thanks goes also to my dearest friends Jonathan Pothuis, Sarah Ashworth, Cristian Santana, dr. Andréa Medina, dr. Claudio Toncelli and Benny Backer who in one way or another changed the course of my life.

I am also grateful to the support of the Programa Formación de Capital Humano Avanzado, CONICYT, BECAS CHILE; grant number: 72111428.

Finally, I want to thank to all people who work in the Product Technology Department and Green Chemical Reaction Engineering Department belonging to the Engineering and Technology institute of Groningen (ENTEG).

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