Since the contents of this chapter can mostly be found in other studies I called it chapter 0.

CHAPTER 0 IMPROVED PROPERTIES OF POLYMERIC MATERIALS BY MEANS OF MIXING TWO POLYMERS.

1 Introduction.

New properties, lower prices and reuse of polymers are needed to meet demands of today's society and therefore of the polymer industry. Polymer is the technical name for what is more generally known as plastic. Plastics are used by almost everybody since (for example) most domestic machines have a housing, which is made out of it. The polymers commonly used in Europe are Polyethylene (PE), Polypropylene (PP), and Polystyrene (PS) (about 25% of the market which is about 500,000 tons per year). These polymers can be extruded without excessive degradation when they contain little impurities. Additives (such as antioxidants) are often added for stabilisation. Other important plastics have more problems with degradation such as in the case of Polyacetals (POM) and Polyamide (PA 6, PA 66, PA 4,6, PA 12, and PA 11). This thesis focuses mostly on reactive compounding of PS, Polyethylene (PE), and PP since a relatively pure stream of PP, PE and PS is most easily obtained. Usually the mechanical properties of the pure blends obtained are poor. However a lot of research has shown that these properties can be brought back to their original level by adding an additional phase (1-17). This phase usually is called the compatibiliser. In this thesis the term alloying agent will be used when a reaction takes place during the compatibilising step.

Polymers are either amorphous or semi crystalline. A semi crystalline polymer has an amorphous and a crystalline part. The part, which is crystalline, has a more or less ordered structure in which the chains of the polymer are often folded in a non random fashion. The mechanical properties of semi crystalline polymers are strongly determined by the crystallites, which usually enhance their stiffness (for example in polypropylene). Amorphous polymers are either very brittle (polystyrene) or very tough (polycarbonate). It is quite difficult to predict the mechanical properties of a semi crystalline material since it is determined by many parameters (such as its percentage of crystallites). It is more feasible to understand the mechanical properties of an amorphous polymer.

Unfortunately the demands for many applications need a set of properties that no polymers can fulfil. One method to satisfy these demands is by mixing two or more polymers. Mixing two or more polymers to produce blends or alloys is a well-established route to achieve a certain amount of physical properties, without the need to synthesise specialised polymer systems. This subject has been the focus of many papers, most of which was empirical. Part of the literature on blends is of academic rather than of commercial interest. Well known examples of commercial blends are high impact polystyrene (HIPS) and Acrylonitrilene-
butadiene-styrene (ABS). These blends are tough and have good processability. However when polymers are mixed the blend often is brittle. One of the most interesting examples of an amorphous polymer is polystyrene because of its brittleness. Adding a compatibiliser with the structure of a copolymer, to PS/PE improves the toughness by a factor 3 (17).

Improving the mechanical properties of polystyrene has been chosen as the aim of this thesis since brittleness is a large disadvantage of polystyrene in many applications. Another application for the results of this thesis is recycling. The first important step for recycling is purification of the plastic stream. The second step is recycling by mixing polymers in such a way that the required properties are reached.

1.1.1 Theory of compatibilisation.

Mechanical properties of polymers and polymer blends are very important in many applications. Significant for these properties is compatibility between the different polymers which is frequently defined as miscibility on a molecular scale of the components of the blend.

Over 300 pairs of miscible polymers are known (14), from which only a few systems have been commercialised such as:
- Polyphenylether/Polystyrene (PPE/PS), Polycarbonate/Polyethyleneterephthalate (PC/PET), and Polycarbonate/Polybutyleneterephthalate (PC/PBT).
- Another type of blend consists of incompatible polymers for which various morphologies can be realised via processing, for instance droplets or fibres in a matrix and stratified or co-continuous structures. The structures induced are usually unstable. For example addition of a rubber to a brittle polymer often creates an unstable morphology, after processing this blend for the second time because the morphology may change.

In most cases, melt mixing two polymers results in blends, which are weak and brittle. The incorporation of a dispersed phase into a matrix mostly leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases. Improving the mechanical properties of a blend is often done by compatibilisation which means modification of normally not miscible blends by mixing a block-copolymer into the blend to improve the miscibility. The end-use performance has been improved many times by this method. However this method is not the same as creating blends, which have miscibility on a molecular scale, or even blends containing very finely dispersed phases. From a practical point of view a blend often is considered to be compatible if a certain set of mechanical properties is achieved.

Well known examples of blends are the impact modified, (rubber) toughened polymers, where polymers with different glass transition temperatures are blended. Many other blends are known such as barrier polymers for packing, where specific polar or apolar polymers are
combined in order to increase the resistance against transport of water and gas (oxygen, carbon dioxide).

It should be kept in mind that several methods are known to improve the properties of plastics. For many polymers additives are needed to improve for example processability and lifetime (lubricants or stabilisers), modulus and strength (mineral fillers such as glass beads, chalk, clay, mica or glass-fibre reinforcement), appearance and colour (pigments), conductivity (conducting fillers such as aluminium flakes or carbon) or flammability (flame retardants). The word compatibiliser will sometime be replaced by alloying agent since a blend with improved mechanical properties is also called an alloy. Therefore this name can also be used since the improvement of the properties of the blend is the purpose of adding or creating a compatibiliser.

1.1.2 Mechanical properties of blends.

The incorporation of rubber particles within the matrix of brittle plastics may enormously improve their impact resistance. Toughening in brittle plastics is also observed under other loading conditions, such as simple low-rate stress-strain deformation and fatigue. When a force is applied to a blend several deformation mechanisms of the major phase and of cracks which are formed in the blend are important. Their relative importance may depend on the polymer and on the nature of the loading. The effect of the quantity of rubber incorporated and the method of forming the blend has been studied extensively for polystyrene/polybutadiene blends. An optimum rubber concentration and phase domain size exists, the values depending on the rubber and polymer concerned. The importance of graft-type bonding and the finer, more complex morphology developed in graft copolymers should be emphasised.

1.2 What has been done in earlier work.

Much work has been done on the blending (mixing) of polymers by many authors. A large part of these studies deal with attempts to obtain a combination of properties of different polymers. Unfortunately the mechanical properties of blends are usually worse instead of better for many combinations of polymers. The conventional methods for improvement of these properties are often expensive and do not always meet the required demands. A small part of the most recent research on compatibilisation and blending will be described shortly here. This is done to obtain some idea of the number of possible choices for application of the method described. In principle compatibilisation is influenced by the molecular weight distribution and concentration of a compatibiliser in the dispersed phase in complex ways to influence final blend properties.
The best known effect from compatibilisation is reduction of the interfacial tension in the melt. This causes an emulsifying effect and leads to an extremely fine dispersion of one phase in the other. A second effect is to increase the adhesion at phase boundaries giving improved stress transfer. For this effect the interaction between the compatibilising copolymer chain and the polymer chains of the dispersed phase and the matrix phase will be important. A third effect is the inhibition of coalescence of the dispersed phase by modifying the phase boundary interface. These and other effects (such as modification of rheology) may occur simultaneously which complicates the ongoing of the whole process.

In the work of Lester and Hope (1) the complexity of the interaction of the compatibiliser with the morphology of a blend was illustrated when high density polyethylene (HDPE) was mixed with nylon 6, nylon 6-6, nylon 6-3T and polyethylene terephthalate (PET), with and without low levels of various proprietary compatibilising agents. The blends were characterised in terms of phase morphology (by scanning electron microscopy, SEM) and by tensile testing of samples cut from moulded plaques. The finest phase dispersion did not guarantee the highest values of ultimate elongation. Compatibilisation of PE/PS blends was studied by Barendsen et al (2) by addition of graft copolymers of LDPE with PS (PS-g-LDPE) to blends of LDPE and PS. Blends were produced by melt mixing at 195 °C on a laboratory mill, and the graft copolymer was first melt blended with the polymer forming the dispersed phase before being added to the matrix polymer. Addition of 7.5 % by weight copolymer caused a substantial reduction in size of the dispersed phase. Heikens et al (3) showed that differences in the detailed fine structure of copolymers gave rise to large effects on the impact strength, and on the magnitude of the tensile modulus of the blends.

Copolymers of Propylene and Ethylene (EP), displaying residual crystallinity because of long ethylene sequences, could serve as compatibilising agents for polypropylene/low-density-polyethylene (PP/LDPE) blends (4). The purely amorphous copolymers were less effective as compatibilising agents. To obtain a linear relationship between tensile strength and composition for HDPE/PP blends 5% addition of ethylene-propylene rubbers (EPR) is necessary (5). However it must be noted that there are many examples in the literature where blends prepared from the same types of polymer behave differently. This is hardly surprising in the light of the high sensitivity of mechanical properties to variation of the temperature, composition, morphology of the blend, etc.

A method commonly used to induce compatibility between polyamides and polyolefines is by chemical modification of the polyolefines. The polyolefines contains pendant carboxyl groups, often by grafting with maleic anhydride (MAH), which forms chemical linkage to the polyamide via the terminal amino groups. The concept has been employed to produce compatibiliser by grafting MAH onto the polyolefine, and then adding the MAH-g-polyolefine as a third component in polyamide/polyolefine blends (6). The existence of a reaction between
the MAH and the nylon 6 amino end groups was established by solvent extraction of the PP phase, estimation of the number of end groups and DSC analysis of the residue. Other approaches to enhance the properties of polyolefine/polyamide blends include the addition of acrylic acid/butyl acrylate/styrene terpolymers to blends of nylon and polyethylene and the addition of nylon 6-polybutene multiblock copolymer to nylon 6/HDPE blends (7-9). Also compatibilisation of nylon 6/PS blends was studied by addition of a Methyl-methacrylate-styrene (MMAS) copolymer (6). The use of a copolymer of styrene (S) and maleic acid (MAH) which is known as SMA was found to be more effective than styrene acrylonitrile (SAN) copolymer in compatibilising nylon 6/PS blends (10). Many studies have been published in which the use of MAH led to interesting results.

The success of using block and graft copolymers as compatibilisers accounts for some of the large number of the commercially available blends: high impact polystyrene (HIPS) and acrylonitrile butadiene styrene (ABS). Methyl-methacrylate (MMA)-graft rubbers and styrene-Methyl-methacrylate copolymer (MMAS)-graft rubbers were blended with ABS increasing fracture toughness in MMA-graft rubbers and decreasing toughness in MMAS-graft rubber. This reduction for MMAS-rubbers increased with increasing Styrene content (11). An increase in toughness of polyamide-6 (PA6) in PA6/SAN blends was found by adding polystyrene-co-maleic anhydride (SMA) (12).

The blend, which is studied most in this thesis, PS/HDPE, is one, which has been studied extensively in the literature either as model of an immiscible blend or for the purpose of development of an economic method for plastic scrap recycling. In the literature, studies of the rheology of the blend showed that the steady state shear flow invariably led to shear segregation of phases and irreproducible results. The dynamic-oscillatory tests were reproducible, indicating the presence of the apparent yield stress due to an interactive morphology. It appeared that the concentration at which the yield stress was the largest depends on the method of sample preparation. This means that the morphology of the blends was not at equilibrium. The structure imposed by compounding was stabilised by the low diffusion rate. This may explain why in spite of the apparent yield stress it was possible to construct time-temperature master curves.

The influence of addition of hydrogenated poly(styrene-b-isoprene) di-block copolymer (SEB) to a blend was studied by Utracki (13). Paul (14) and Barlow (15) reviewed the use of block copolymers and other copolymers to the compatibilisation of immiscible polymer blends. The effect of Kraton 1652G (containing PS and copolymer of ethylene and butane) or EPCAR 847 (containing ethylene-propylene-ethylene nortere copolymer) are of particular interest. Addition to PET/HDPE blends variously affected the different physical properties, modulus and yield strength. In general, addition of block copolymers of the same chemical nature as the two homopolymers of a blend is an obvious choice which, when optimised, will lead to enhancement of properties. The disadvantage of this method is on one hand their
inaccessibility and the lack of flexibility in tuning the properties to specific applications. A way of dealing with these problems is using multicomponent and/or multiphase material. Their utility varies from system to system, as a function of their compatibilising efficiency and the overall performance of the final product.

Shilov et al (16) analysed the composition of an immiscible blend as a function of linear dimensions. Between a domain of polymer A and a domain of polymer B exists an interfacial layer. For some blends this layer may have a final thickness as large as 4 nm. The interfacial region can be considered as a third phase. This phase has been stabilised in many commercial polymer alloys via selective crosslinking, resulting in reproducibility of performance, processability, and recyclability. The thickness of the interface layer depends on the thermodynamic interactions, macromolecular segment size, concentration, and phase conditions. The interfacial tension, and the domain adhesion characterise the interface. The interfacial tension is the integral of the Helmholtz free energy change across the interface, which gradually changes over the interfacial area from phase A to phase B, due to a changing composition of the third phase between both phases.

Much more systems as described here have been studied, but also a few other approaches have been used. One approach was to blend incompatible polymers in the presence of a free radical initiator, like a peroxide. The aim, for the radical from the initiator, is to attack the polymer chains of the dispersed phase of the blend. This only has a limited success because the addition of peroxide did not seem to have a significant compatibilising effect. In chapter 1 an idea is proposed which has a few of the same characteristics but will show to be more effective and to have much more possibilities. In this (new) method the radical present on these chains in turn may combine with monomers dissolved in the dispersed phase to form a copolymer which is the "in situ" created compatibiliser. The elongation at break obtained with the method described in this thesis in chapter 9 and 10 will be compared with the results described in the thesis of E.Kroeze (17). More literature of PS/PE blends can also be found in (17).

Polymer blends can be produced directly in several types of reactors. Production of a blend, on a macroscopic scale is done by coextrusion to produce multi-layered structures via casting, blowing, blow moulding and injection-moulding. Extrusion (melt) blending is in principle a rather flexible method. Unless specific interactions exist phase separation of the major and minor phase of the blend occurs, which is the case for a very large part of the possible combinations of polymers. Many blend microstructures are possible for which only the simple case of a spherical dispersed phase mixed in a major phase will be studied here.
2 This thesis.

This thesis deals with many subject such as incompatible pairs of polymers, processing conditions, compatibilisation and the morphology of the blends obtained. Aiming at controlling the properties of the blend a special method of blending polymers has been studied. The phase morphology will normally not be in thermodynamic equilibrium, however in most cases it will be stabilised against de-mixing because the blend has been compatibilised. This blend then is studied by quenching the blend to a temperature below the glass transition temperature of one or both phases. Stabilisation of the blend could also been achieved via the occurrence of crystallinity in one or both phases, or sometimes by crosslinking. In chapter 1 of this thesis a new method, different from the ones investigated before, is proposed. To investigate this method particular attention will be paid to the polystyrene/polyethylene blend as a model system. The same method can also be used for most combinations of bulk or engineering polymers, aimed at high performance applications (for instance aerospace products).

The different subjects are treated separately in 10 chapters. In chapter 1 the idea developed in this thesis is explained and some results are shown. The 3D-flow in the mixing and transporting section and the 3D-temperature profile have been modelled to be able to develop a computer code which describes how this method works in a continuous single-step production process in the extruder. This is done by solving the Navier-Stokes and the energy equations in the geometry of the intermeshing corotating twin screw extruder (APV, MPF-50) (chapter 2, 3, and 4).

During reactive compounding mass transfer by diffusion of monomers and initiators occur both in the dispersed phase of the blend and in its neighbourhood. Some diffusion coefficients have been measured which is described in chapter 5. They have been measured for molecules comparable to initiators as TrigonoX (peroxide, AKZO-Nobel). Also the formation of a graft copolymer in the dispersed phase during mass transfer of monomer out of the dispersed phase is studied as described in chapter 5.

The melting, heating, and mixing of polymers in an extruder have been studied experimentally and theoretically in chapter 6 and 7. During mixing the minor phase deforms to a long stretched shape which after some time breaks up into small spheres. Usually deformation of the dispersed phase of the blend occurs rapidly. In our method of reactive compounding in the intermeshing corotating twin screw extruder, polymerisation of the monomer and modification of the polymer chains of the dispersed phase and the matrix phase occur in the dispersed phase.

A computer model has been developed, which will be described in chapter 8, enabling us to describe the process of reactive blending in the extruder. To do so the size of the dispersed phase of a blend, the conversion of monomer added into the blend, and the molecular weight distribution of the formed graft-copolymer are calculated. The models developed for reactive
compounding were used to establish the optimal screw geometry and working domain. These results have been used to select the experimental conditions.

In chapter 9 and 10 the production of a polystyrene/high density polyethylene (PS/HDPE) is described for which the elongation at break improved by a factor 20. The blends produced also showed an enormous improvement in their toughness and Notched Izod impact values. It is remarkable that the properties of the PS/PE and PS/PP blends that are obtained by chemical modification of the dispersed phase are comparable with the properties of HIPS.

The influence of the blending/extrusion parameters on the properties of the blend was also studied. Rheology, processing, compatibilisation, reactions and heat and mass transfer are some of the subjects, which will be dealt with in the method developed and studied. However since these subject are all of interest they have all been studied sufficiently for describing our method of reactive blending in an extruder. Due to a lack of time it was not possible to deal with all the subjects in more detail. Therefore additional studies are needed to further improve the results which will be described in this thesis. The measured mechanical properties in this thesis are average values of at least four samples usually with a range of experimental error within 5%. The glass transition temperature, melt transition temperature and the conversions usually are average values of 3 experiments. All percentages of the dispersed phase and monomer are in weight percentage in this thesis. In chapter 8, 9 ,and 10 the conversion has been calculated which means the conversion of the monomer inside the dispersed phase. From the results obtained it seems likely that the chemical adhesion between the matrix and the dispersed phase of the blend plays a key role in the improvement of the mechanical properties of the alloys that have resulted from this investigation.

References.