Chapter 3

Wood adhesive emulsions from thermosetting alternating polyketones

Abstract

Aqueous polymer emulsions were prepared by chemical modifications of thermosetting alternating polyketones in a single one-pot reaction. Polymeric amines derived from the polyketones can act as polymeric surfactants for the self-emulsification of thermosetting polyketones. The stability and structure of the resulting emulsions with respect to the storage time at room temperature (20 °C) at different experimental conditions were thoroughly studied by dynamic light scattering, rheology, and Cryo-SEM. Emulsions with an average particle size smaller than 1 μm and a viscosity less than 1 Pa s could be achieved and remained stable for at least 2 years. The prepared emulsions were qualified as wood adhesives for the wood composite industry, according to the European Standard for wood adhesive testing.

Keywords: Polyketones; Wood adhesives; Polymeric surfactants; Water emulsions

3.1 Introduction

Thermosetting polyketones, produced by alternating co- and ter- polymerization of carbon monoxide, ethylene, and propylene, constitute a relatively new class of viscous low molecular weight resins. Due to the presence of highly active carbonyl groups, thermosetting polyketones can be cured in a variety of ways, e.g. conversion to polyfurans, reduction to poly-alcohol, co-condensation with commercial formaldehyde resins, etc. The Paal-Knorr reaction, involving pyrrole ring formation between an amino group and two adjacent carbonyl groups, has been used as basic cross-linking chemistry for these materials. In this curing reaction, water-resistant pyrrole units are formed with the elimination of water, using a variety of di- or multi-functional amino-based curing agents. Based on this curing chemistry, thermosetting polyketones can be used in various areas like coatings, foaming, adhesives, and polymer composites. However, thermosetting polyketones display a relatively high viscosity and therefore can be difficult to directly apply on a substrate. In this respect and also because of the environmental restrictions on organic solvent-based systems, the development of waterborne dispersions or emulsions is the preferred route for the application of thermosetting polyketones.

Polymeric emulsions in water are generally produced by using surfactants or direct emulsion polymerization. In recent years, block and graft structured polymeric surfactants were used to replace low molecular weight ones in a variety of applications as emulsifiers, dispersion stabilizers, wetting agents, and compatibilizers. Copolymers consisting of hydrophilic and hydrophobic blocks, may exhibit interesting properties, such as self-assembly, micelle-formation, surface absorption, and molecular association. In the previous chapter, the synthesis of a new family of polymeric amines (polyamines) by chemical modifications of polyketones via the Paal-Knorr reaction has been described. Interesting properties in aqueous solution (e.g. micelle-formation, long-term stability of the formed micelles, high surface activity, and fluorescence) were observed for these polyamines. Thus, they may hold great promise for many applications, such as emulsifier, drug carriers, cation exchange resins, pharmaceuticals, and photoluminescent materials. In the present work we report a simple route to prepare water-borne polyketone emulsions, using the protonated polyamines as polymeric surfactants, previously derived by the modifications of polyketones. This approach not only allows to combine all different processing steps in a single one-pot reaction, but also represents a very economical way to disperse polyketones in water.

The use of water-based polyketone dispersions as adhesives in the wood composite industry such as plywood, particleboard, fiberboard, and wood panels is currently seen as the most promising application of polyketones. Dominant wood adhesive systems used in
the market are nowadays based on urea-formaldehyde or phenol-formaldehyde. However, both of these adhesives are based on formaldehyde, a known hazardous chemical and suspected carcinogen to the human health.\textsuperscript{15-17} Thus there is an increasing need to develop formaldehyde-free and environmental-friendly wood adhesives. Polyketone-based emulsions do not release any volatile toxic components during the processing steps and the byproduct of all emulsification steps (including the polyketone modifications) is only water.

In this work we systematically investigated the different factors that have an effect on the stability and structure of the emulsions (i.e. emulsification conditions, protonation level and amount of polyamines, the molecular weight and ethylene content of the polyketones to be emulsified) by determining the particle size and viscosity of the emulsions up to the storage time of 2 years at room temperature (20 °C). The morphology of the emulsions was studied by Cryo-SEM. According to the European Standard (EN-314) for wood adhesive testing, the quality of the emulsions applied as wood adhesives was evaluated by measuring the shear strength on hard wood (maple) substrates.

### 3.2 Experimental

**Materials.** The alternating polyketones with 0% ethylene (PK0, Mw-1680), 30% ethylene (PK30, Mw-3970), and 50% ethylene (PK50, Mw-5350) based on the total olefin content, were synthesized, according to a previously reported procedure.\textsuperscript{1-2} 1,2-diaminopropane (Acros, 99%) and acetic acid (Acros, ≥99.7%) were purchased and used as received.

**Emulsion preparation.** The emulsions were prepared by using the following procedure (Figure 3.1). Initially, chemical modifications of the PK30 (we denote with mPK30, the initial weight of the PK30 undergoing the modification reaction) with 1,2-diaminopropane were carried out to prepare polyamines in a sealed 250 ml round bottom glass reactor with a reflux condenser, U-type anchor impeller in an oil bath. Details of the procedure and successive protonation were described in Chapter 2. After modifications, 70% of the carbonyl groups have been converted to pyrrole rings (determined by potentiometric titration), thus meaning that only 30% of the carbonyl groups remain unreacted. During the emulsification step, a second quantity of unmodified polyketones (PK0, PK30, and PK50) and de-ionized milli-Q water were added into the protonated polyamine solutions for a final fixed 50 wt% solids resin composition (the amount of water was corrected for the amount of water developed during the polyamine synthesis). All these different steps were carried out in a single one-pot reactor. The obtained emulsions were stored in sealed high
density polyethylene (HDPE) containers at room temperature for a period of up to 2 years and analyzed at regular intervals.

Figure 3.1 Scheme of the preparation of aqueous polymeric emulsions based on thermosetting polyketones.

**Dynamic light scattering.** The dynamic light scattering (DLS) measurements were performed on a Zetasizer 5000 instrument (Malvern Instruments, UK) at a wavelength of 633 nm and at a temperature of 25 °C. Scattered light was detected at a 90 degree angle. The viscosity of (0.89 mPa s) and the refractive index (1.33) of water at 25°C were used for data analysis. The intensity autocorrelation functions obtained from the DLS were analyzed using CONTIN algorithm in all the measurements. The apparent hydrodynamic diameter, \( D_H \), was obtained using the Stokes-Einstein relation:

\[
D_0 = kT / 3\pi \eta D_H
\]

where \( D_0 \) is the diffusion coefficient, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( \eta \) is the viscosity of the solution. All samples were diluted with deionized milli-Q water prior to the measurements.

**Rheological analysis.** The viscosity of the emulsions was measured with an AR 1000 rheometer (TA Instruments, USA), using an aluminum cone-and-plate fixture of 2° and 40 mm in diameter. The apparent viscosity of the samples was measured at a constant shear rate of 15 s\(^{-1}\). The viscosity-shear rate relationship was measured as the shear rate was increased from 5 s\(^{-1}\) to 60 s\(^{-1}\). All experiments were carried out at 20 °C.

**Cryo scanning electron microscopy (Cryo-SEM).** The Cryo fixation technique was used to prepare the samples for SEM observation. A cold field emission scanning electron microscope (JEOL 6301 F) equipped with an Oxford CT 1500 HF Cryotransfer system
Wood adhesive emulsions was used. A drop of diluted (four times) emulsions was placed on a piece of freshly cleaved mica surface and was Cryo fixated into a liquid nitrogen slush at -210 °C after blotting of the drop to a thin layer. After transport of the specimen-holder with the sample into the Cryotransfer system, surface water was removed by sublimation for 10 min and a 3 nm thick coating of Au/Pd was sputtered at -120 °C. SEM micrographs of the samples were recorded at -120 °C.

**Wood adhesive testing.** The hard wood maple veneers for adhesive testing were vacuum dried at 105 °C for 10 h to reduce moisture content. Salicylic acid (0.5 wt% based on the second quantity of polyketones, i.e. PK0, PK30 or PK50) was added into the emulsions as curing catalyst. According to the European Standard (EN-314) for wood adhesive testing, the emulsions were applied as 150 g/m² single adhesive line onto one side of the hard wood maple veneer (a thickness of 4 mm, dimension of 50 mm×25 mm) and adhesive line for each piece veneer sample was 25 mm×25 mm (Figure 3.2). The lapped two pieces of glue-applied veneer was hot-pressed for 5 min at 200 °C under a 3 MPa constant pressure. After hot-pressing, the samples were subjected to immersion in boiling water for a period of 72 h. The shear strength of the samples (previously cooled down but on purpose not dried) was tested on an Instron 4301 machine using 5 kN power sensor with a crossing head speed 2 mm/min. The shear strength is defined as the load required to break the specimen, divided by the area of the adhesive bonds. At least 10–13 replicates were performed for each experiment series with standard deviation less than 0.3 MPa.

![Figure 3.2 Lapped specimen for shear strength test.](image)

### 3.3 Results and discussion

#### 3.3.1 Emulsification

The influence of different factors on the emulsification process and the resulting average particle size (Table 3.1) was first investigated. As can be seen in Figure 3.3a, the particle size decreases initially with the mixing time and then it levels off after roughly 40 min. To obtain an emulsion, sufficient energy input is required to overcome the interfacial tension between the two fluids and mechanically break up large droplets into smaller ones. The
observed trend clearly indicates that the equilibrium particle size is reached after 40 min mixing time. A descending trend is observed when plotting the particle size as a function of the rotor speed (Figure 3.3b). In this case we observe a clear decrease of particle size as function of the rotor speed, which we can roughly estimate as proportional to the mechanical energy input. This is actually not surprising and in agreement with the general principles of emulsion formation.\textsuperscript{18} It is remarkable that the emulsions can be prepared even with a very low energy input (10 min, 300 rpm). In general, an important aspect in the preparation of polymeric emulsions is to obtain an average droplet size lower than 1 µm and a narrow size distribution in order to ensure high kinetic stability. Here, average particle size lower than 1 µm can be achieved by simply increasing the energy input either at higher rotor speed or at longer emulsification time. By comparing Figure 3.3a and Figure 3.3b, it can be seen that energy density, which is the mechanical energy input per unit volume of the zone where the droplets are disrupted, plays a more important role in the emulsification process than the total energy input. The influence of the emulsification temperature shows an interesting behavior (Figure 3.3c). The particle size remains almost constant below 50 °C and starts to increase up to several micrometers when the temperature rises to 70 °C. The latter effect is probably due to the increased thermal energy that favors eventually re-coalescence of the droplets.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotor speed</td>
<td>Rpm</td>
<td>300-1300</td>
</tr>
<tr>
<td>Emulsification time</td>
<td>Min</td>
<td>10-90</td>
</tr>
<tr>
<td>Emulsification temperature</td>
<td>°C</td>
<td>25-70</td>
</tr>
<tr>
<td>Protonation level of the polyamines</td>
<td>%</td>
<td>40-80</td>
</tr>
<tr>
<td>Polyamine content (PK0/mPK30, PK30/mPK30 or PK50/mPK50)</td>
<td>weight ratio</td>
<td>1-2</td>
</tr>
<tr>
<td>Polyketone grade or ethylene content</td>
<td>%</td>
<td>0-50</td>
</tr>
</tbody>
</table>

Table 3.1 Investigated factors for the emulsification step.
Figure 3.3 Effect of (a) mixing time (500 rpm, 50 °C); (b) rotor speed (1 h, 50 °C); (c) emulsification temperature (500 rpm, 1 h) on the particle size of the emulsions (60% protonation level, PK30/mPK30=1.5).
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The particle size is also related to the kind of polyketones employed for the emulsification (Figure 3.4). According to the general theory of emulsion formation, the average diameter of particles dispersed in the matrix is proportional to the viscosity of the dispersed phase.\textsuperscript{18} Low ethylene content is usually related to a lower molecular weight of the polyketones and therefore a lower viscosity of the dispersed phase. On the basis of this, it is reasonable to assume that the observed effect (particle size increasing with ethylene content) might be simply related to the difference in viscosity. The particle size of the emulsions is also influenced by the protonation level and amount of the employed surfactants (polyamines) (Figure 3.5). It is found that a low protonation level results in a much smaller particle size. This effect is correlated with the nature and the aqueous properties of the polyamines. In general, surfactants play two main roles during the emulsification: (i) they lower the interfacial tension between the two different phases to facilitate droplet break-up; (ii) they prevent re-coalescence. It is already known that polyamines at low protonation level display higher surface activity.\textsuperscript{14} In addition, as the protonation level of the polyamine increases (higher than 60\%) the polyamines start to dissolve into water molecularly and act more like polyelectrolytes instead of surfactants. The particle size increases also with the PK30/mPK30 ratio. This is an expected trend, since the amount of surfactants determines the total interfacial area and the decrease of the PK30/mPK30 ratio causes a better stabilization of the interface. The most striking result in the emulsification studies is that the use of the polyamines even at low protonation level (40\%, 50\%) and high PK30/mPK30 ratio of 2 can still result in emulsions with an average particle size in the order of 500 nm.

![Diagram](image)

**Figure 3.4** Effect of ethylene content of the second quantity polyketones and polyamine content on the particle size of the emulsions (500 rpm, 1 h, 50 °C, 60% protonation level).
Figure 3.5 Effect of protonation level and polyamine content on the particle size of the emulsions (500 rpm, 1 h, 50 °C).

The particle size distributions of the emulsions can also be effectively varied by adjusting the protonation level of the polyamines and the PK30/mPK30 ratio (Figure 3.6). A narrow and mono-modal distribution can be achieved at low protonation level and low PK30/mPK30 ratio. The evolution of the particle size distribution is worth noticing here. The narrow distribution is gradually transformed into broad distribution and even to asymmetric bimodal with the increase of the PK30/mPK30 ratio (Figure 3.6a). The same trend of the particle size distribution can also be observed as a function of increasing protonation level (Figure 3.6b). In this case the width of the distribution increases with the protonation level, probably as consequence of the lower surface activity of the polyamines at high protonation levels.

Figure 3.6 Effect of (a) PK30/mPK30 ratio (60% protonation level); (b) protonation level (PK30/mPK30=1.5) on the particle size distribution of the emulsions (500 rpm, 1 h, 50°C).
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In order to obtain a more quantitative correlation between the particle size and the different factors outlined above, we summarized all our results in a statistical model. In this case, we used a multivariable, not-linear regression technique to be able to express the average particle size ($y$) as function of the mentioned experimental parameters ($x$’s). The resulting model has the following form:

$$y = \sum (f_{ij} * x_i^2 + f_{2i} * x_i) + f_0$$  \hspace{1cm} (2)$$

where the summation is extended over all investigated factors namely: protonation level ($x_1$), polyamine content ($x_2$), rotor speed ($x_3$), emulsification temperature ($x_4$), ethylene content ($x_5$), and emulsification time ($x_6$). The $f_{ji}$ (j=1,2; i=1-6) are the corresponding coefficients determined by the fitting procedure. The $f_0$ represents the intercept of the model.

We first started to check the validity of the model by the analysis of variance (Table 3.2). The very low P-value indicates that the model is statistically significant (confirmed also by the random distribution of the residuals, not shown here for brevity) and that the observed differences are not due to a random noise of the experimental data. The $R^2$ value of the model is 0.941 with an adjusted $R^2$ value of 0.909, thus indicating that there is a reasonable agreement between the model itself and the experimental data. The latter is also confirmed by the plot of predicted vs. experimental values (Figure 3.7). Once established that the model is statistically significant and describes reasonably the experimental data, we calculated the value of the regression coefficients (Table 3.3). Combination of the $f$-values with the equation (2) reported above, yields the equation for the developed model immediately. The latter allows easy prediction of the particle size as functions of the employed experimental conditions.

<table>
<thead>
<tr>
<th></th>
<th>Sum of squares</th>
<th>Degrees of Freedom</th>
<th>Mean Square</th>
<th>Point of F-distribution</th>
<th>P-value</th>
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<tr>
<td>Model</td>
<td>$1.741 \times 10^7$</td>
<td>12</td>
<td>$1.450 \times 10^6$</td>
<td>27.716</td>
<td>$3.661 \times 10^{-10}$</td>
</tr>
<tr>
<td>Error</td>
<td>$1.099 \times 10^6$</td>
<td>21</td>
<td>$5.233 \times 10^4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>$1.850 \times 10^7$</td>
<td>33</td>
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</table>

Table 3.2 Analysis of variance (ANOVA) for the statistical model.
### Table 3.3 Values of the regression coefficients.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor name</th>
<th>$f_{ii}$</th>
<th>$f_{2i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>Protonation level</td>
<td>1.174</td>
<td>-83.648</td>
</tr>
<tr>
<td>$x_2$</td>
<td>Polyamine content</td>
<td>-463.177</td>
<td>2.725×10³</td>
</tr>
<tr>
<td>$x_3$</td>
<td>Rotor speed</td>
<td>4.07×10⁻⁴</td>
<td>-1.212</td>
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<tr>
<td>$x_4$</td>
<td>Emulsification</td>
<td>2.849</td>
<td>-226.44</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x_5$</td>
<td>Ethylene content</td>
<td>0.417</td>
<td>-11.814</td>
</tr>
<tr>
<td>$x_6$</td>
<td>Mixing time</td>
<td>0.147</td>
<td>-21.419</td>
</tr>
<tr>
<td></td>
<td>Intercept</td>
<td>$f_0=3.975×10³$</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.7** Plot of predicted vs. experimental values.

#### 3.3.2 Emulsions stability

The stability or life-time of emulsions is considered a primary requirement for a wide variety of industrial applications of emulsions. It could be examined from the phase separation by visual inspection and the change of particle size with respect to storage time. After 2 month storage, it was observed that only the emulsions with the particle size higher than 2 µm (protonation level of 80% with PK30/mPK30≥1.75 and protonation level of 60% with PK30/mPK30 = 2) experienced phase separation by visual examination (left part in Figure 3.8). However no sigh of phase separation can be observed for the samples at low protonation level (40-50%) after a storage time of 2 years (right part in Figure 3.8).
The effect of storage time on the particle size was studied at different protonation levels by using several polyketone grades. The obtained emulsions are kinetically stable at least for one year and their average particle size slightly increases to a small extent over that period of time (Figure 3.9). The monomodal particle size distribution becomes slightly broader over the same time period. By comparison of the graphs at different protonation levels, we did not find any immediate correlation between the experimental conditions upon which an emulsion is formed and its stability. In general, the instability of emulsions arises from the processes of creaming (or sedimentation), Ostwald ripening, flocculation, and coalescence. They may take place concurrently at different rates leading eventually to complete phase separation if equilibrium is achieved. Creaming or sedimentation rate depends on droplet size, the density difference between the dispersed and continuous phases, continuous phase viscosity, and interdroplet interactions. The phase separation of emulsions with large particles here may result from creaming or sedimentation. Ostwald ripening and coalescence is the process whereby larger droplets grow at the expense of smaller ones depending on the solubility and diffusion rate of the dispersed phase in the continuous phase. Small particle size is against sedimentation (or creaming) because of the Brownian motion. Consequently, the diffusion rate is higher than the sedimentation (or creaming) rate induced by the gravity force. Thus, it can be believed that the slight increase of particle size with time can be attributed to Ostwald ripening which is also the main instability mechanism for emulsions of submicron particle size.20

Figure 3.8 Pictures of the emulsions: left sample at 80% protonation after 2 month storage; right sample at 40% protonation after 2 years storage (PK30/mPK30=2, 500 rpm, 50 °C, 1 h).
It must be stressed here that the two general mechanisms of emulsion stabilization (i.e. electrostatic and steric repulsion) are probably both active in our system and responsible for the observed stability. The polyamines contain both positive charges (due to the protonation) as well as hydrophilic polymer chains which can significantly extend in water. A quantitative estimation of these effects is difficult to achieve due to the extreme complexity of the emulsions in terms of chemical composition and molecular weight distribution of the starting polymers. In terms of the effect of ethylene content of the second polyketones, it can be seen that particle size also grows bigger after one year, but on a very small scale (Figure 3.10). We must notice again substantial stability of the particle size as function of time with no remarkable difference as a function of the ethylene content. It is worth noticing the lack of any significant change in particle size of the emulsions for the samples at low protonation level (i.e. 40%, 50%) even after 2 year storage (Figure 3.11).
Figure 3.10 Effect of storage time on the particle size of emulsions (a) use of PK50 as second polyketones; (b) use of PK0 as second polyketones (60 % protonation, 500 rpm, 1 h, 50 °C).

Figure 3.11 Effect of storage time on the particle size of emulsions for a period of 2 years (1300 rpm, 1 h, 50 °C, PK30/mPK30=1.5).
Cryo-SEM studies of the emulsion morphology (Figure 3.12) after 6 months’ storage time indicate uniform spherical shape and narrow particle size distribution of the particles at both low and high magnification. The average particle size of the emulsions at two different protonation levels (50% and 60%) is around 400 nm and 800 nm respectively. It can also be seen that the size distribution of the particles in Figure 3.12b is also much broader than that in Figure 3.12a. These observations from the Cryo-SEM are strikingly agreement with the results from the DLS measurements.

Figure 3.12 Cryo-SEM images of the emulsions at (a) 50% protonation level at low and high magnification; (b) 60% protonation level at low and high magnification (500 rpm, 1 h, 50 °C, PK30/mPK30=1.5).
3.3.3 Rheology

The rheology of the emulsions was also studied at different protonation levels, polyamine content, and ethylene content of the polyketones. The rheological properties of emulsion-based materials play a major role in determining their suitability for particular applications. In terms of wood adhesives, it may be desirable to control the viscosity in view of the applying methods on the wood surface, such as the use as a paste or spraying. Furthermore, rheological studies can provide useful information on the stability and internal microstructure change of emulsions. We first report in Figure 3.13 the viscosity as a function of the storage time for two different protonation levels, namely 40% and 50%. It can be seen that there is a dramatic decrease in viscosity after 1 week and then no significant change within the storage time up to one year. The long term stability (i.e. after the first week) is in agreement with the particle size measurements discussed above. The sharp decrease of viscosity during the first week is not explainable in terms of average particle size or particle size distribution, since the latter do not change significantly.

![Figure 3.13](image)

**Figure 3.13** Effect of storage time on the viscosity of the emulsions at (a) 40% protonation level; (b) 50% protonation level (500 rpm, 1 h, 50 °C).

As a result one might speculate that a rearrangement of the polymers within each particle is taking place with the surfactant migrating at the interface and possibly retreating a part of his chains from the water solution in the first week (Figure 3.14). Due to the solubility of (highly) protonated chains in water only the gray particles in the picture are actually seen by the dynamic light scattering technique used for particle size measurements. This hypothesis has in first instance a chemical basis. Potentiometric titrations show that a fully protonated polyamine in de-ionized water gives a pH of about 4.5, thus indicating that the ammonium groups easily deprotonate in water. This would mean that as soon as the surfactant is in de-ionized water, a slight deprotonation of the former at the surface should take place. As a result the chains become more hydrophobic and thus less keen to be solubilized in water. One might speculate that in the beginning all the
highly protonated chains will stretch in water while later, due to deprotonation or even proton exchange with the amino groups close to the surface, some of them will retract and come closer to the hydrophobic surface of the polyketone particle. Thus, we could see none or little difference in the particle size as measured by the light scattering, but observe a difference in viscosity.

![Representation of chain retraction for the emulsions.](image)

**Figure 3.14** Representation of chain retraction for the emulsions.

The mechanism of arms-retraction is indirectly but substantially confirmed also by another experimental evidence. The fresh samples reveal a non-Newtonian or pronounced shear thinning flow behavior (Figure 3.15). Slow transition from a non-Newtonian to a Newtonian behavior, with viscosity independent of the shear rate, is observed with respect to storage time. Such transition might be explained by the retraction of the polymeric chains (previously stretched into the water solution) on the surface of the polymer particle. Indeed, shear thinning behavior is typical of polymeric systems in the melt and related to chain entanglements. In the beginning the system (left part of Figure 3.14) is composed of particles at high concentration (50 wt% of total polymers in water) which will form entanglements between the chains by overlapping. On the other hand, as the systems rearranges in time (right part of Figure 3.14), the overlap between the chains and the number of entanglements diminishes, resulting in a Newtonian-like behavior. This is very similar to what is reported in the literature for polystyrene-end-capped polyelectrolytes\(^ {22}\), where a transition from non-Newtonian to Newtonian behavior has also been observed as a function of concentration. Thus most probably the arm retraction causes dis-entanglement of the polymer chains between different particles, leading to the observed rheological properties. Apart from the exact mechanism of the emulsion formation and stability, it is worth noticing that a low viscosity less than 1 Pa s could be achieved at high solid content (50 wt%) even after 1 year storage time. An increase in the PK30/mPK30 ratio is accompanied by a pronounced reduction in the viscosity at all protonation levels. This may be attributed to an increase in the effective volume fraction with increasing particle size, caused by the increase of the PK30/mPK30 ratio.
At 60% and 80% protonation level, viscosity decreases initially after one week storage and then increases up to the point when emulsions become gel-like materials (Figure 3.16). These effects may be related to the associative behavior of the used polymeric surfactants and polyketone complex aggregates. However, up to now, the microstructure and the association mechanism of these polymers in aqueous solutions are still unclear. Water-soluble amphiphilic polymers can also possess bulk-thickening properties when compared with conventional surfactants. The polyamines may act as thickening agents to increase the viscosity with time. Another possible explanation is that the amino groups of the polyamines may slowly react with the second quantity of the polyketones at room temperature and therefore lead to low cross-linking density, which cause the viscosity to increase with time. The latter hypothesis was confirmed by studying the viscosity of the emulsions in the presence of the curing catalysts (0.5 wt% salicylic acid based on second polyketones) as functions of time at room temperature and different protonation levels (40%, 50%, and 60%). It was found that the presence of the curing catalysts could result in a much higher viscosity compared with the emulsions without catalysts. This strongly indicates that the increase in viscosity can be explained by a chemical reason and namely the cross-linking mechanism proposed above, which could be both intra- and inter-particle. In case of the effect of ethylene content of the second polyketones, similar rheological behavior of the PK0 and PK50 can be observed as that of the PK30. This is in agreement with the particle size measurements discussed above.
Wood adhesive emulsions

Figure 3.16 Effect of storage time on the viscosity of the emulsions at (a) 60% protonation level; (b) 80% protonation level (1 h, 500 rpm, 50 °C).

3.3.4 Wood adhesive testing

The polyketone based emulsions can be easily applied and evenly spread at maple wood surface (left part of Figure 3.17). During the curing reactions in the hot press, water starts to evaporate and the polyamines at this stage act as curing agents to react with the second polyketones in presence of curing catalysts (salicylic acid) leading to water-resistant and stable bis-pyrrole units. The shear strength of the adhesive bonds has been studied on the maple substrates, according to the European Standard (EN-314), a 72-hours boiling water test. In this test, wood swells into all the directions in water and the adhesive must be able to withstand all these forces. Furthermore, the adhesive itself is tested on the hydrolysis, water adsorption, and thermal stability. The samples must fail by giving wood failure and contain fibers from the opposite veneer, indicating that wood adhesives are stronger than wood (right part of Figure 3.17). The shear strength should be higher than 1 MPa, which is the standard value of the EN-314. It has been proven that all tested emulsions pass the EN-314 with significantly higher shear strength values (almost 3 times of the standard value of the EN-314) (Figure 3.18). It is also found that protonation level and PK30/mPK30 ratio have no significant effect on the shear strength of the emulsions within the employed range. The adhesion is most probably related to the reaction at the surface between the carbonyl groups (mostly of the second virgin polyketones) and the hydroxyl groups present on the wood. In this respect it is reasonable to assume that the polyamines mainly act as surfactants and curing agents in this system and do not play an important role in terms of interaction with wood. Indeed only 30% of the carbonyl groups remain unreacted after reaction with the di-amine, and those remaining ones have obviously a high steric hindrance with respect to the “virgin” carbonyl groups of the second polyketones. When tested again after two months’ storage time, similar shear strength data as compared to freshly prepared adhesives was obtained. This illustrates the long shelf-life of the
polyketones based adhesives, prepared according to the procedures described above. The wood adhesive test was also performed for a sample after the storage time of 2 years (Figure 3.18). It is surprising to observe that the performance of the polyketone-based emulsions remains the same as the fresh ones when applied as wood adhesives.

Figure 3.17 Spread of the polyketone based emulsions on the wood surface before hot-pressing (left) and the ruptured sample after shear strength test (right).

Figure 3.18 Effect of protonation level, storage time, and PK30/mPK30 ratio on the shear strength of wood adhesives (1 h, 500 rpm, 50 °C).
3.4 Conclusions

Aqueous polymer emulsions are produced by chemical modifications of thermosetting polyketones in a one-pot laboratory procedure. The properties of the resulting emulsions are dependent on the emulsification process, the protonation level and the quantity of the in-situ polymeric surfactants (polyamines). A multivariable, non-linear regression model has been developed in order to determine the effect of each experimental parameter on the resulting average particle size of the emulsions. The same model allows easy prediction of the particle size as functions of the experimental conditions. The prepared emulsions exhibit extremely long shelf life at room temperature (20 °C) and remain stable for at least 2 years. The average particle size, as measured by dynamic light scattering, remains basically the same while the viscosity of the system decreases in the first week and then levels off to a almost constant value. A hypothetical mechanism, which is able to explain this behavior, has been proposed. It involves a kind of “arms” (free polymer chains) retraction of the polyketone particles with respect to time. A direct proof of such mechanism is very difficult to obtain due to the complexity of the system. However, the hypothesis is substantiated both by the considerations on a deprotonation mechanism and viscosity measurements (the latter showing a clear transition from non-Newtonian to Newtonian behavior). When the emulsions are applied as a wood adhesive, a high shear strength can be achieved, which far exceeds the requirement of 1 MPa as demanded by the European Standard (EN-314).

3.5 References