Aqueous Polymer Emulsions by Chemical Modifications of Thermosetting Alternating Polyketones

Youchun Zhang, A. A. Broekhuis, F. Picchioni

Department of Chemical Engineering/Product Technology, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

ABSTRACT: Aqueous polymer emulsions were prepared by chemical modifications of thermosetting polyketones in a one-pot reaction. Polymeric amines derived from the polyketones can act as polymeric surfactants for the self-emulsification of polyketones. The stability and structure of the 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 1-year. The prepared emulsions were qualified as wood adhesives for wood composite industry, according to the European Standard for wood adhesive testing. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3237–3247, 2007

Key words: polyketones; wood adhesives; polymeric surfactants; water emulsions

INTRODUCTION

Thermosetting polyketones, produced by alternating co- and ter-polymerization of carbon monoxide, ethene and propene, are a new class of viscous low molecular weight resins.[1,2] Depending on the molar ratio of ethene and propene, the consistency of thermosetting polyketones varies from viscous flowing materials at room temperature for ethene-free materials to waxy, soft solids at 50% ethene based on the total olefin content. Because of the presence of highly active carbonyl groups, chemical curing of thermosetting polyketones can be carried out in a variety of ways, for example conversion to polyfurans, reduction to poly-alcohol and cocondensation with commercial formaldehyde resins.[3] The Paal-Knorr reaction, involving pyrrole ring formation between an amino group and two adjacent (in γ-position) carbonyl groups, has also been used as basic crosslinking-chemistry for these materials.[4–6] 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 familiar to the epoxy-resin technology. On the basis of this curing chemistry, thermosetting polyketones can be used in various areas like coatings, foams, adhesives, and composites. All these application areas require relatively fast cure chemistry, easy handling and the absence or control over volatile and toxic components. However, thermosetting polyketones display a relatively high viscosity and therefore can be difficult to apply directly on a substrate. In this respect, the development of waterborne dispersions or emulsions, also because of the environmental restrictions on organic solvent-based systems, is the preferred route for the application of thermosetting polyketones.[6–9]

Polymeric emulsions in water are generally produced by using surfactants or direct emulsion polymerization.[10] 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.[11,12] Copolymers consisting of hydrophilic and hydrophobic blocks, may exhibit interesting properties, such as self-assembly, micelle-formation, surface absorption, and molecular association.[13] In a previous study,[14] a new family of polymeric amines (polyamines) has been synthesized by chemical modifications of polyketones via the Paal–Knorr reaction. The resulting polyamines have N-substituted 2,5-pyrrolediyl groups incorporated in the backbone with an amino functional group (either primary, secondary, tertiary, or aromatic) pendant from the main chain. Interesting properties in aqueous solution, e.g., micelle-formation, long-term stability of the formed micelles, high surface activity, and fluorescence, were observed for the polyamines. As such, they may hold great promise for many applications, such as emulsifier, drug carriers, cation exchange resins, in pharmaceutical, and

Correspondence to: A. A. Broekhuis (a.a.broekhuis@rug.nl.).

photoluminescent materials. In the present work we report a simple route to prepare waterborne polyketone emulsions, using the protonated polyamines, previously derived by polyketone modifications, as polymeric surfactants. Such an approach allows not only to combine all different processing steps in a single one-pot reaction, but represents obviously also a economical way to achieve a water emulsions. The use of water-based polyketone emulsions as adhesives in the wood composite industry such as plywood, particleboard, fiberboard, and wood panels is currently seen as the most promising application. Dominant wood adhesive systems used in the market nowadays are based on urea-formaldehyde or phenol-formaldehyde. However, both these adhesives are based on formaldehyde, a known hazardous chemical and suspected carcinogen to the human health.[15–17] Thus there is an increasing need to develop formaldehyde free and environmentally friendly wood adhesives. Polyketone-based emulsions do not release volatile toxic components during any processing step and the byproduct of the emulsification step (including the polyketone modification) is only water.

In this work we systematically investigated the several different factors that have an effect on the stability and structure of the emulsions (emulsification conditions, protonation level and amount of polyamines, the molecular weight and ethene content of the polyketones for emulsification) by determining the particle size and viscosity of the emulsions up to 1-year storage time 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 as wood adhesives was evaluated by measuring the shear strength on hard wood (maple) substrates.

EXPERIMENTAL

Materials

The alternating polyketones with 0% ethene (PK0, M_w-1680), 30% ethene (PK30, M_w-3970) and 50% ethene (PK50, M_w-5350), based on the total olefin content, were synthesized, according to a previously reported procedure.[1] 1,2-Diaminopropane (Acros) and acetic acid (Acros) were used as received.

Emulsion preparation

The emulsions were prepared by using the following procedure (Fig. 1). Initially, chemical modifications of the PK30 (we denote with mPK30 the intial weight of the PK30 undergoing the modification reaction) was carried out to prepare polyamines in a
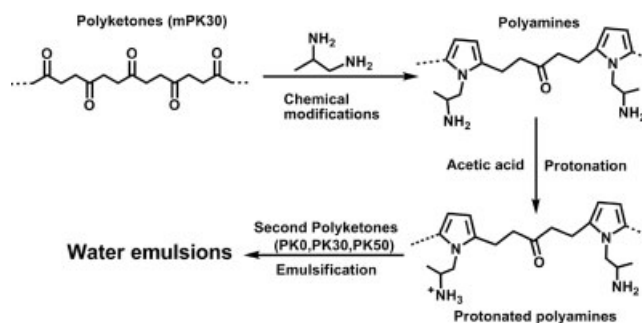
Figure 1 Preparation of aqueous polymeric emulsions based on thermosetting polyketones.

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 are reported elsewhere.[14] After modification, 70% of the carbonyl groups have been converted to pyrrole rings (determined by potentiometric titration[14]), thus meaning that only 30% of the carbonyl groups remain unreacted. During the emulsification step, a second quantity of unmodified polyketone (PK0, PK30, or PK50) and deionized 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 1-year and analyzed at regular intervals.

Dynamic light scattering

Dynamic light scattering measurements were performed on a Zetasizer 5000 instrument (Malvern Instruments, U.K.) at a wavelength of 633 nm and a temperature of 25°C. Scattered light was detected at a 90° angle. The viscosity (0.89 mPa·s) and the refractive index (1.33) of water at 25°C were used as reference for data analysis. To obtain the intensity average hydrodynamic diameter, the autocorrelation data were analyzed using the CONTIN algorithm. The apparent hydrodynamic diameter, D_H, was obtained using the Stokes-Einstein relation:

$$D_0 = \frac{kT}{3\pi\eta D_H} \tag{1}$$

where D_0 is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solution. All samples were diluted with deionized milli-Q water before the measurements.
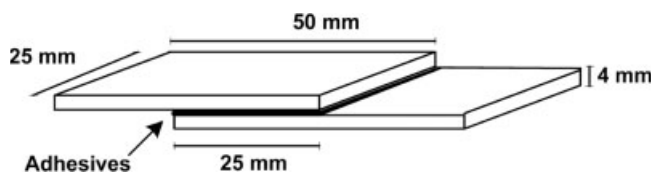
Figure 2 Lapped specimen for shear strength test.

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 to 60 s^{-1}. All experiments were carried out at $20°C$.

Cryo scanning electron microscopy

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 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/m^2 single adhesive line onto one side of the hard wood maple veneer with a thickness of 4 mm, dimension of $50 \times 25 \text{ mm}^2$ and adhesive line for each piece veneer sample was $25 \times 25 \text{ mm}^2$ (Fig. 2). The lapped two pieces of glue-applied veneer was hot-pressed for 5 min at $200°C$ under the 3 MPa constant pressure. After hot-pressing, the samples were subjected to immersion in boiling water for 72 h. The shear strength of the samples (previously cooled down but on purpose not dried) were tested on an Instron 4301 machine using 5 kN power sensor with a crossing head speed 2 mm/

min. Ten to thirteen replicates were performed for each experiment. The shear strength is defined as the load required to break the specimen, divided by the area of the bond.

RESULTS AND DISCUSSION

Emulsification

The influence of different factors on the emulsification process and the resulting average particle size (Table I) was first investigated. As can be seen in Figure 3(a), 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 to overcome the interfacial tension between the two fluids is required to mechanically break up large droplets into smaller ones. The observed trend clearly indicates that the equilibrium particle size is reached after 40 min. A slightly similar (descending) trend is observed when plotting the particle size as a function of the rotor speed [Fig. 3(b)]. 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.[18] It is remarkable that the emulsions can be prepared even with a low energy input (10 min, 300 rpm). An important aspect in the preparation of emulsions is to obtain an average droplet size lower than 1 µm and a narrow size distribution to ensure high kinetic stability. Average particle size lower than 1 µm can be achieved by increasing the energy input either at higher rotor speed or at longer emulsification time. It can be seen, by comparing Figure 3(a,b), 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 [Fig. 3(c)]. The particle size remains almost constant below $50°C$ and starts to increase to several micrometers when the temperature rises to $70°C$. The latter effect is

TABLE I
Investigated Factors for the Emulsification Step

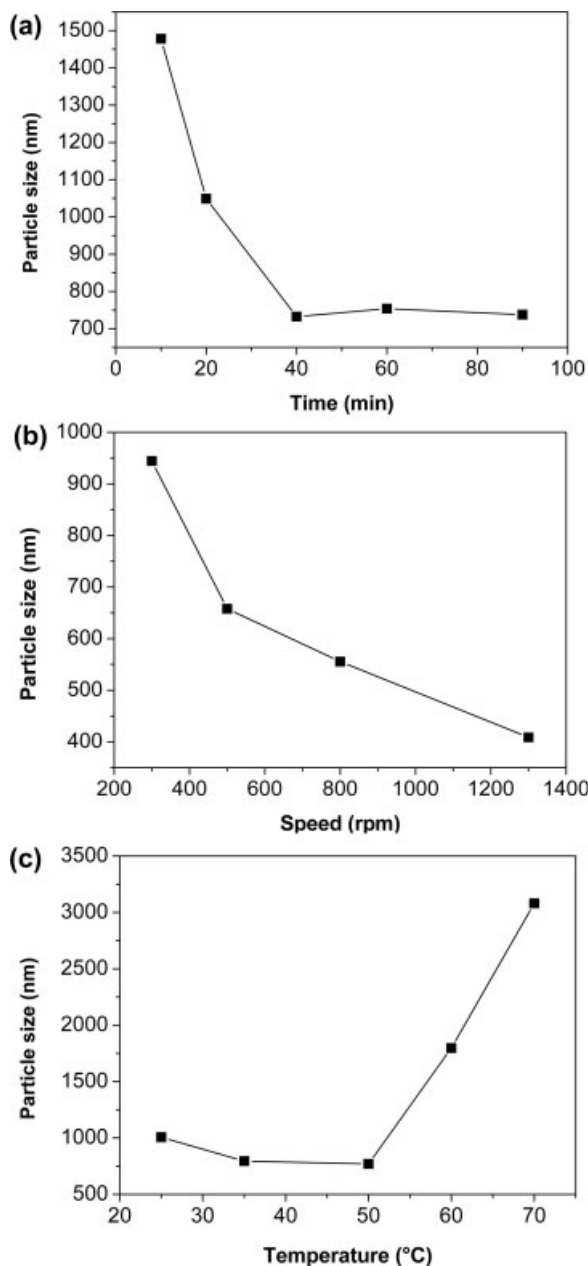| Factors	Unit	Range
Rotor speed	Rpm	300–1300
Emulsification time	Min	10–90
Emulsification temperature	°C	25–70
Protonation level of the polyamines	%	40–80
Polyamine content (PK0/mPK30, PK30/mPK30 or PK50/mPK50 weight ratio)	weight ratio	1–2
Polyketone grade or ethene content	%	0–50

Figure 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).
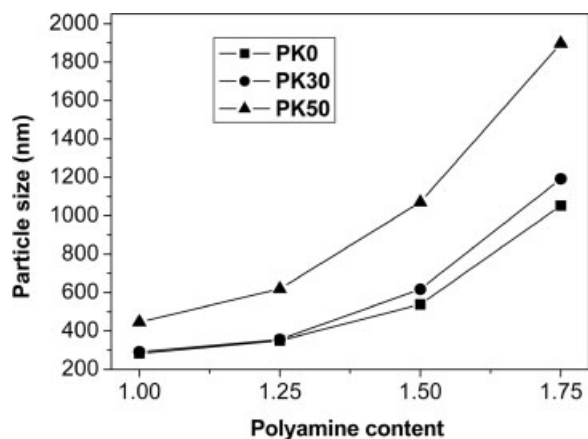

Figure 4 Effect of ethene content of the second quantity polyketones and polyamine content on the particle size of the emulsions. (500 rpm, 1 h, 50°C, 60% protonation level).

assume that the observed effect (particle size increasing with ethene content) might be simply related to the differences in viscosity. The particle size of the emulsions is also influenced by the protonation level and amount of the employed surfactants (polyamines) (Fig. 5). It is found that a low protonation level results in a much smaller particle size. This effect is related to the nature and the aqueous properties of the polyamines. In general, surfactants play two main roles during the emulsification: they lower the interfacial tension between the two different phases to facilitate droplet break-up and they prevent recoalescence. It is already known that polyamines at low protonation level display higher surface activity.[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/
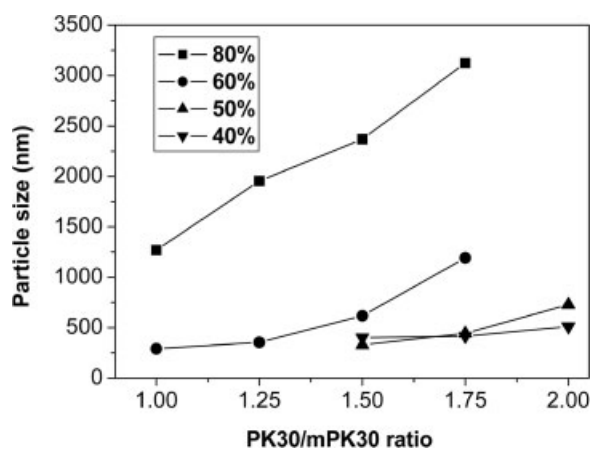
probably due to the increased thermal energy that favors eventually recoalescence of the droplets.

The particle size is also related to the kind of polyketones employed for the emulsification (Fig. 4). Low ethene content is usually related to a lower molecular weight of the polyketones and therefore a lower viscosity of the dispersed phase. According to the general theory of emulsion formation, the maximum diameter of particles dispersed in the matrix is proportional to the viscosity of the dispersed phase.[18] On the basis of this it is reasonable to

Figure 5 Effect of protonation level and polyamine content on the particle size of the emulsions. (500 rpm, 1 h, 50°C).
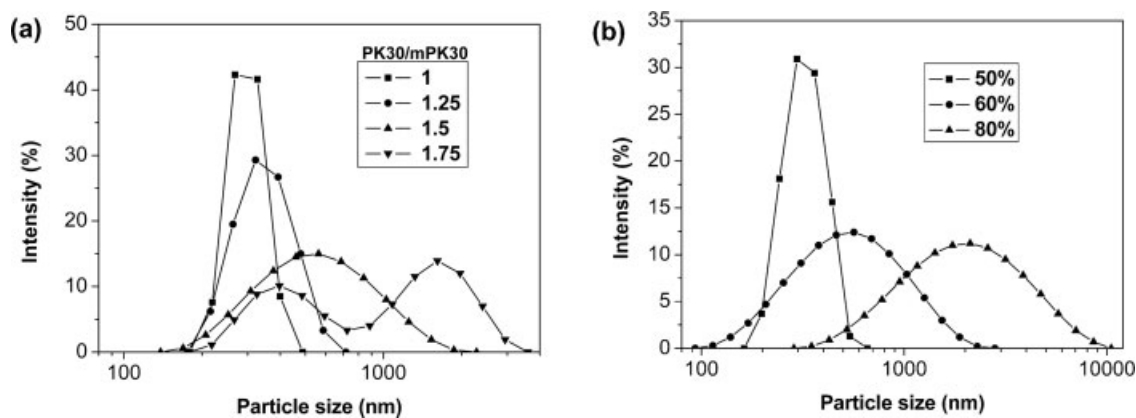
Figure 6 Effect of (a) PK30/mPK30 ratio (60% protonation level); (b) protonation level (PK30/mPK30 = 1.5) on the particle size distribution of the emulsions. (500 rpm, 1 h, 50°C).

mPK30 ratio. This is the expected trend since the amount of surfactants determines the total interfacial area and the decrease of the PK30/mPK30 ratio cause 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. The particle size distribution of the emulsions can also be effectively varied by adjusting the protonation level of the polyamines and the PK30/mPK30 ratio (Fig. 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 [Fig. 6(a)]. The same trend of the particle size distribution can also be observed as a function of increasing protonation level [Fig. 6(b)]. Also 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.

To obtain a more quantitative correlation between the particle size and the different factors outlined earlier, we summarized all our results in a statistical model.[19] 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:

$$y = \sum_i \left(f_{1i} \times x_i^2 + f_{2i} \times x_i \right) + f_0 \qquad (2)$$

where the summation is extended over all investigated factors and namely: protonation level (x_1), polyamine content (x_2), rotor speed (x_3), emulsification temperature (x_4), ethene 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, f_0 representing the intercept of the model. We first started to check the validity of the model by the analysis of variance (Table II). It is clear from the low P-value that the model is statistically significant (confirmed also by the random distribution of the residuals, not shown here for brevity) and it is 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 versus experimental values (Fig. 7). Once established that the model is statistically significant and describes reasonably the experimental data, we calculated the value of the regression coefficients (Table III). Combination of the f-values with eq. (2) reported earlier, immediately yields the equation for the developed model. The latter allows easy prediction of the particle size as function of the employed experimental conditions.

TABLE II
Analysis of Variance (ANOVA) for the Statistical Model

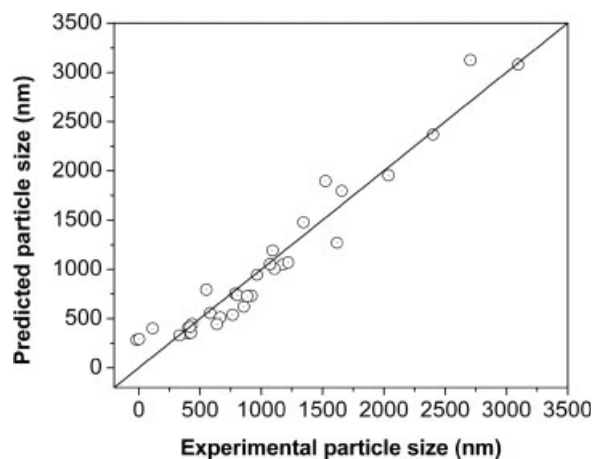|	Sum of squares	Degrees of Freedom	Mean Square	Point of F-distribution	P-value
Model	1.741×10^7	12	1.450×10^6	27.716	3.661×10^{-10}
Error	1.099×10^6	21	5.233×10^4		
Total	1.850×10^7	33			

Figure 7 Plot of predicted versus experimental values.

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 from the change of particle size with respect to storage time. After 2 month storage, it is 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) experience phase separation by visual examination; however no sight of phase separation can be observed for the rest of samples after 1-year storage (Fig. 8). The effect of storage time on the particle size is studied at different protonation levels by using several polyketone grades. The obtained emulsions are kinetically stable at least for 1-year and their average particle size slightly increases to a small extent over that period of time (Fig. 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, floc-

culation, 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 and consequently the diffusion rate are 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 submicron particle size.[20] It must be stressed here that the two general mechanisms of emulsion stabilization[21] (i.e., by electrostatic and steric repulsion) are probably both active in our system and responsible for the observed stability. The polyamines contain indeed both positive charges (because of the protonation) as well as hydrophilic polymer chains which can significantly extend in water. A quantitative estimation of these effects (currently under investigation) is difficult to achieve because of 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 ethene content of the second polyketone, it can be seen that particle size also grows bigger after one year, but on a small scale (Fig. 10). We must notice again a substantial stability

Figure 8 Pictures of the emulsions: left sample at 80% protonation after 2 month storage; right sample at 50% protonation after 1-year storage. (PK30/mPK30 = 2,500 rpm, 50°C, 1 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
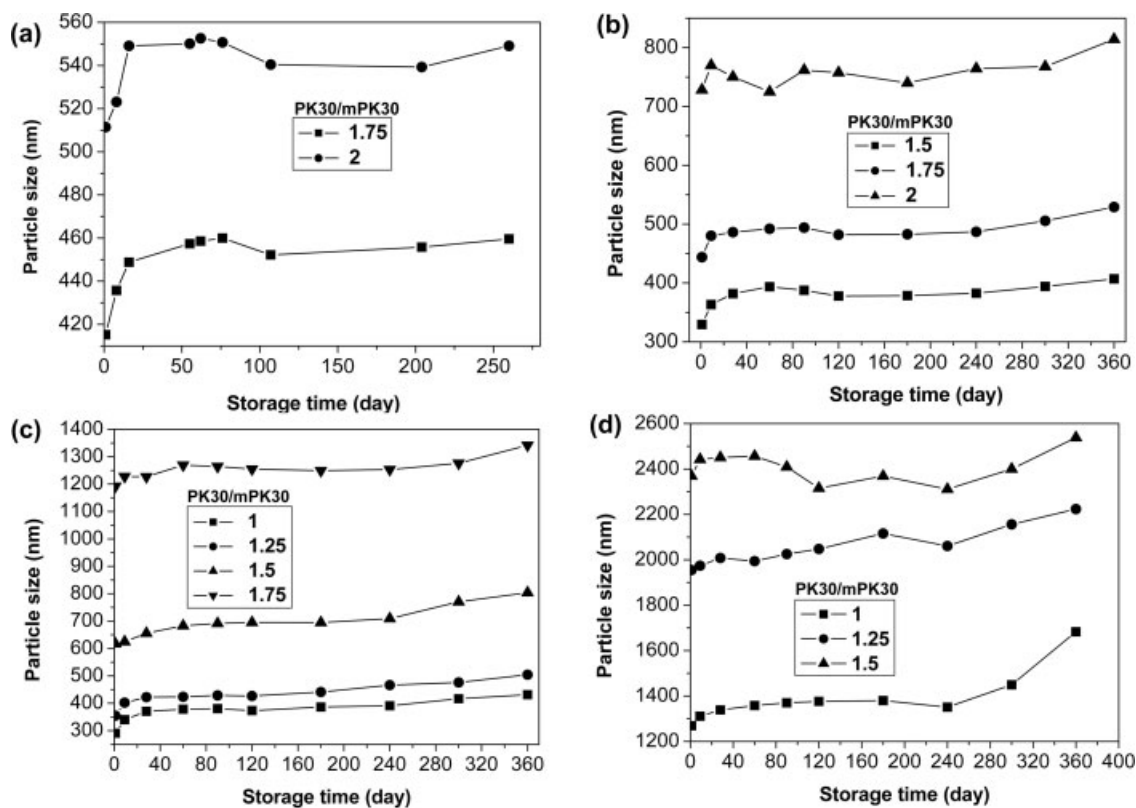
TABLE III
Values of the Regression Coefficients

Factor	Factor name	f_{1i}	f_{2i}
x_1	Protonation level	1.174	−83.648
x_2	Polyamine content	−463.177	2.725×10^3
x_3	Rotor speed	4.07×10^{-4}	−1.212
x_4	Emulsification temperature	2.849	−226.44
x_5	Ethene content	0.417	−11.814
x_6	Mixing time	0.147	−21.419
Intercept		$f_0 = 3.975 \times 10^3$	

Figure 9 Effect of storage time on the particle size of the emulsions at (a) 40% protonation level; (b) 50% protonation level; (c) 60% protonation level; (d) 80% protonation level. (500 rpm, 1 h, 50°C).

of the particle size as function of time with no remarkable difference as a function of the ethene content.

Cryo-SEM studies of the emulsion morphology (Fig. 11) after 6 months' storage indicate uniform spherical shape and narrow particle size distribution of the particles at both low and high magnification. The average particle size of emulsions at two different protonation levels (50 and 60%) is around 400 and 800 nm respectively. It can also be seen that size distribution of the particles in Figure 11(b) is also much broader than that in Figure 11(a). These observations from the Cryo-SEM are strikingly in agreement with the results from the dynamic light scattering measurements.

Rheology

The rheology of the emulsions was also studied at different protonation levels, polyamine content, and ethene content of the polyketone. The rheological properties of emulsion-based materials play a major
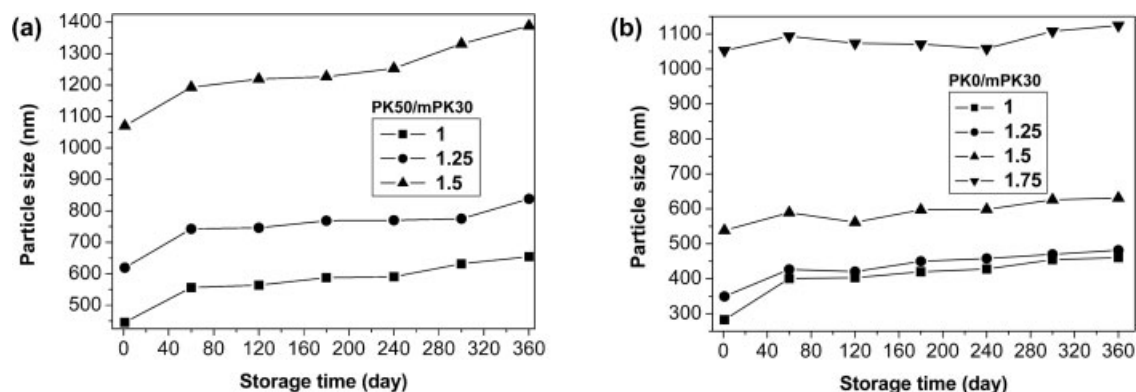

Figure 10 Effect of storage time on the particle size of emulsions (a) using PK50 as second polyketones; (b) using PK0 as second polyketones. (60% protonation, 500 rpm, 1 h, 50°C).
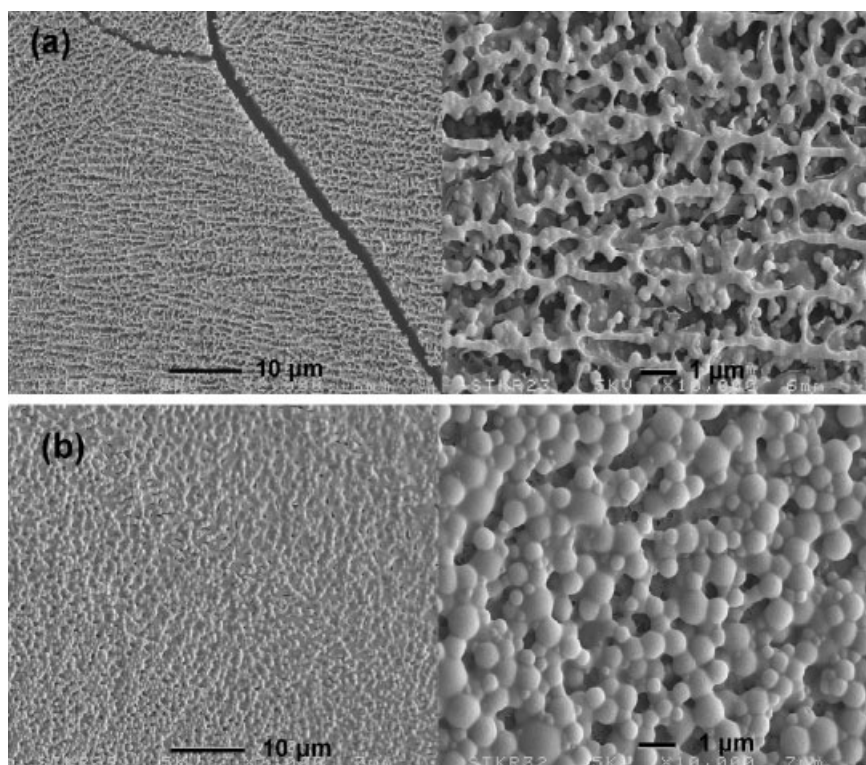
Figure 11 Cryo-SEM images of the emulsions at (a) 50% protonation level at low and high magnification; (b) 60% protonation level at low and high magnification. (500 rpm, 1 h, 50°C, PK30/mPK30 = 1.5).

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 12 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 distribution discussed earlier. 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. 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 (Fig. 13). Because of the solubility of (highly) protonated chains in water only the gray
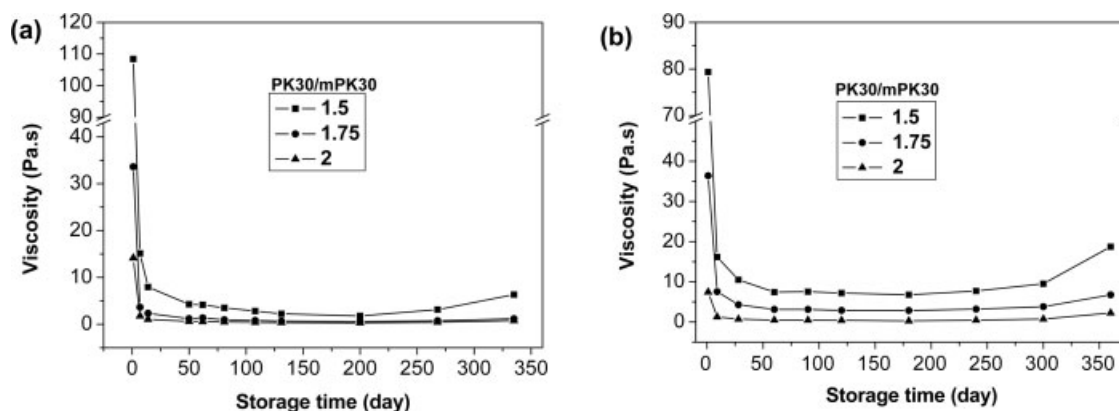

Figure 12 Effect of storage time on the viscosity of the emulsions at (a) 40% protonation level; (b) 50% protonation level. (500 rpm, 1 h, 50°C).
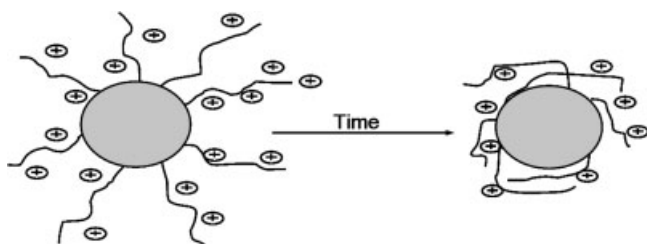
Figure 13 Representation of chain retraction for the emulsions.

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 deionized water gives a pH of about 4.5, thus indicating that the amonium groups easily deprotonate in water.[14] This would mean that as soon as the surfactant is in deionized water, a slight deprotonation of the former should take place. This has the fact that the chains become more hydrophobic and thus less keen to be solubilized in water as a first direct consequence. One might speculate that in the beginning all the highly protonated chains will stretch in water while later, because of 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. As a result one would see none or little difference in the particle size as measured by the light scattering, but measure a difference in viscosity. Such 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 (Fig. 14). 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 Fig. 13) is composed of particles at high concentration (50 wt % of total polymers in water) which, by overlapping, will form entanglements between the chains. On the other hand, as the systems rearranges in time (right part of Fig. 13), the overlap between the chains and the number of entanglements diminishes, resulting in a Newtonian-like behavior. This is similar to what is reported in the literature for polystyrene-end-capped polyelectrolytes[22] where also a transition from Newtonian to non-Newtonian behavior has been observed as func-

tion of concentration. Thus most probably the arm retraction causes de-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 the 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 1-week storage and then increase to a large amount and emulsions become gel-like materials with time (Fig. 15). 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 crosslinking 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 a catalyst (0.5 wt % salicylic acid based on second polyketones) as a function of time at room temperature and different protonation levels (40, 50, 60%). It was found that the presence of cure-catalysts could result in a much
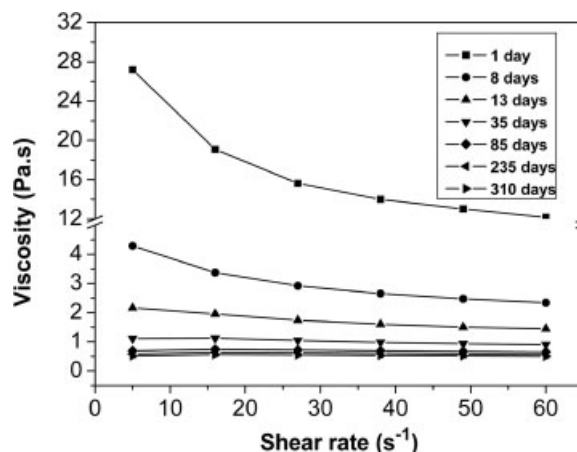

Figure 14 Effect of shear rate on the viscosity of the emulsions. (50% protonation level, 500 rpm, 1 h, 50°C, PK30/mPK30 = 1.5).
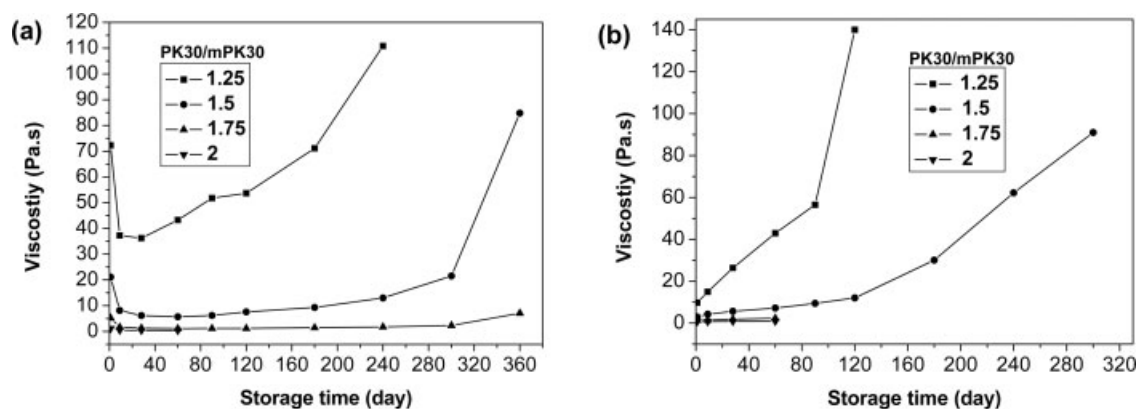
Figure 15 Effect of storage time on the viscosity of the emulsions at (a) 60% protonation level; (b) 80% protonation level. (1 h, 500 rpm, 50°C).

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 crosslinking mechanism proposed above, which could be both intra- and interparticle. In case of the effect of ethene content of the second polyketones, similar rheological behavior can be observed as that of the PK30. This is in agreement with the particle size measurements discussed earlier.

Wood adhesive testing

The polyketone based emulsions can be easily applied and evenly spread at maple wood surface (left part of Fig. 16). 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 catalysts and lead 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-h boiling
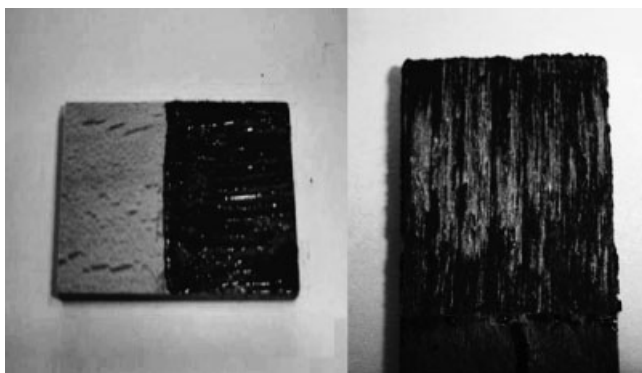
water test. In this test, wood swells into all the directions in water and the adhesive must be able to withstand all these forces. Furthermore, the adhesive itself is tested on the hydrolysis, water adsorption, and thermal stability. The samples must fail by giving wood failure and contain fibers from the opposite veneer, indicating that wood adhesives are stronger than wood (right part of Fig. 16). 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 significant high shear strength (Fig. 17). It is 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 (which acts mainly as
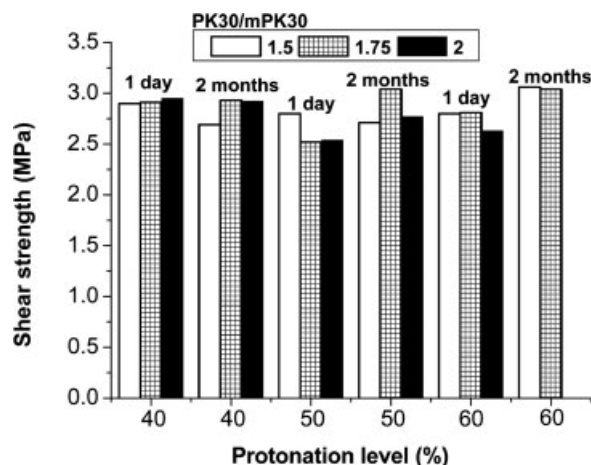

Figure 16 Spread of the polyketone based emulsions on the wood surface before hot-pressing (left) and the failured sample after shear strength test (right).

Figure 17 Effect of protonation level, storage time, and PK30/mPK30 ratio on the shear strength of wood adhesive. (1 h, 500 rpm, 50°C).

surfactant in this system) does not play an important role (and thus also the protonation level). Indeed only 30% of the carbonyl groups remain unreacted after reaction with the diamine, and those remaining 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 adhesive was obtained. This illustrates the long shelf-life of the polyketones based adhesives prepared according to the procedures described earlier.

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, nonlinear regression model has been developed 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 1-year. 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. 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 difficult to obtain because of the complexity of the system. However, the hypothesis is substantiated both by the consider-ations 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 exceeds the requirement of 1 MPa as demanded by the European Standard (EN-314).

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