

The Structure and Properties of Acrylic-Polyurethane Hybrid Emulsions and Comparison with Physical Blends

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Received 11 May 1999; accepted 16 December 1999

ABSTRACT: Aqueous acrylic-polyurethane hybrid emulsions were prepared by semi-batch emulsion polymerization of a mixture of acrylic monomers (butyl acrylate, methyl methacrylate, and acrylic acid) in the presence of polyurethane dispersion. Equivalent physical blends were prepared by mixing acrylic emulsion and polyurethane dispersion. The weight ratio between acrylic and polyurethane components varied to obtain different emulsion properties, microphase structure, and mechanical film properties of hybrid emulsions and physical blends. Particle size and molecular mass measurements, scanning electron microscopy, glass transition temperature, and rheological measurements performed characterization of the latex system. The mechanical properties were investigated by measuring tensile strength and Koenig hardness of dried films. The experimental results indicate better acrylic-polyurethane compatibility in hybrid emulsions than in physical blends, resulting in improved chemical and mechanical properties. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 67–80, 2000

Key words: water-borne coatings; acrylic emulsion; polyurethane; hybrid; blend

INTRODUCTION

Water-borne polymer emulsions are an important class of materials, especially in the paint and coating industry. Increasing concern for health, safety, and the environment has driven many researchers to prepare water-borne polymers with sophisticated composition and architecture, which are expected to exhibit almost the same performances as conventional solvent-borne systems.

Acrylic (AC) emulsions and polyurethane (PU) aqueous dispersions have been used extensively in coatings applications. Both systems have some disadvantages such as reduced film formation, lower chemical resistance, coarse mechanical properties of acrylic, a high cost, low pH stability, and limited outdoor durability of PU.¹ To improve

the properties of an individual polymer system it is common to mix them. Better mechanical stability, solvent and chemical resistance, and toughness are obtained from the PU portion. Outdoor resistance, pigmentability, and lower cost are due to the AC component. Direct blending of AC emulsion and PU dispersion results in films with properties of lower quality to those predicted by the “rule of mixtures,” because of limited compatibility between PU and polyacrylate.

An alternative approach to the physical mixing of AC emulsion and PU dispersion is the emulsion polymerization of AC monomers in the presence of aqueous PU dispersion called “hybrid process.” When using this approach AC monomers swell into the particles of PU dispersion and increase the ability of mixing of these two polymers.²

Hirose and Kadowaki³ found that it is possible to develop water-borne emulsions with superior performances by producing emulsions with a multi-phase structure in each emulsion particle with different techniques, such as core-shell poly-

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Journal of Applied Polymer Science, Vol. 78, 67–80 (2000)
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merization type, seeded polymerization technology or formation of interpenetrating network.

Hegedus and Kloiber^{1,4} observed that formation of the so-called “hybrid” particles is the result of in situ polymerization of the respective monomers and prepolymers. PU is formed by step-growth polymerization, whereas polyacrylate is formed by free radical chain-growth polymerization. Therefore AC and PU segments are not directly attached through primary bonds. The presence of hybrid particles is the result of numerous entanglements and secondary intermolecular bonding forces (hydrogen bonding, dipole-dipole interactions, etc.). The process appears to result in interpenetrating network (IPN) formation of AC and PU chains at the molecular level.

Bontinck et al.⁵ observed that the simplest combination of AC and PU is a physical blend. When both polymers consist of a cross-linked network, an IPN is formed. These IPNs show a lower amount of phase separation than physical blends. A more complicated approach involves preparing the new hybrid system by chain extension of the PU in the presence of AC, or the opposite, by emulsion polymerization of AC monomers in the presence of PU. To obtain a storage stable AC-PU dispersion, the emulsification and/or dispersing mechanism of both polymers must be compatible within the desired pH-range, usually of 7–8.

Many techniques described in the literature have been used to determine the miscibility of polymer blends.⁶ The most widely used criterion relies on the measurement of the glass transition temperature (T_g). The detection of a single glass transition temperature, with value somewhere between the T_g 's of individual polymers indicates a miscible system. Conversely, a nonmiscible system will exhibit two T_g 's corresponding to the T_g 's of individual components. The term “miscible” is used to describe the blends that are homogeneous at the molecular level. Various equations have been made to relate the T_g of miscible blends to blend composition. Couchman and Karasz proposed the following relationship⁶:

$$\ln T_g = \frac{\sum_i w_i \Delta c_{pi} \ln T_{gi}}{\sum_i w_i \Delta c_{pi}} \quad (1)$$

where Δc_{pi} is the change in specific heat of the i -th component at the glass transition temperature T_{gi} and w_i represents the mass fraction of i -th component. Eq. (1) may be simplified⁷:

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (2)$$

where T_g , T_{g1} , and T_{g2} , are the glass transition temperatures of the blend, homopolymer 1, and homopolymer 2, respectively. In the case of an immiscible system, the T_g 's of the two phases can render some information on whether there is partial miscibility between the two components. For a completely immiscible system, the T_g 's of the two phases in the blend should be equal to the T_g 's of the respective pure polymers. A shift in T_g of the polymer in the blend, with respect to the pure polymer, may indicate some degree of miscibility. The shift can be used to quantify the amount of one polymer dissolved into the other one in a two-phase blend.

The rheological properties of latex systems are of both practical importance and theoretical interest. Most practical uses of latexes in processing and in various coatings applications require the control of viscosity. Some latex may exhibit Newtonian behavior with constant viscosity, independent of shear stress or shear rate. However, the viscosity of many liquids and emulsions are dependent on shear rate (Non-Newtonian). The pseudoplastic or shears thinning emulsions show decrease of viscosity with increasing shear rate. Many dispersions, including latex systems, may exhibit complex viscoelastic rheological properties.^{8,9}

There are some patents^{10–14} on AC-PU hybrid emulsion synthesis, and only a few available publications discussing the behavior and fundamental properties of these emulsions.^{1–5} To contribute to these investigations, our work is oriented to AC-PU hybrid emulsions prepared by emulsion polymerization of AC monomers in the presence of PU dispersion. The objective of the study is to compare the chemical and mechanical properties of hybrid emulsions and blends of equivalent chemical compositions.

EXPERIMENTAL

Chemicals

As the AC component, a mixture of butyl acrylate (BA; BASF) and methyl methacrylate (MMA; BASF) in ratio of 1:1 was used together with an AC acid (AA; BASF). As the initiator water soluble potassium persulfate (Peroxide Chemie) was used. The emulsifier TRITON XN 45 S (ammonium alkylphenoxypolyethoxy sulfate) was supplied

Table I Recipe for Preparing AC Emulsion

Component	Initial Charge (g)	Preemulsion (g)	Initiator Solution (g)
Butyl acrylate BA		240.0	
Methyl methacrylate MMA		240.0	
Acrylic acid AA		2.5	
Potassium persulfate	0.3		1.5
Emulsifier	1.7	14.0	
Distilled water	220.0	230.0	50.0
Preemulsion	50.0		

by Union Carbide. The chemicals were of commercial purity and were used without further purification. The aqueous PU dispersion was a commercial anionic polyester carbonate (Industrial Copolymers).

Synthesis of AC Emulsion

MMA/BA/AA copolymer particles were prepared by the semibatch emulsion polymerization process. The basic recipe is given in Table I. The polymerization was carried out under an inert nitrogen atmosphere in a 2-L glass reactor, equipped with a reflux condenser, stirrer, thermometer, and addition funnels. Emulsifier was dissolved in distilled water charged to the reactor at 60°C. A part of separately prepared preemulsion and potassium persulfate was added and the initial charge was heated to 80°C. The initial charge reacted at 80°C for 15 min to obtain the emulsion seeds. Then the remaining preemulsion and initiator solution were fed in two separate streams at constant flow rates of 6.26×10^{-2} g/s and 4.77×10^{-3} g/s, respectively, for 3 h. The emulsion was then neutralized with 25% ammonia solution.

Preparation of AC-PU Physical Blends

Physical blends including same proportions of AC and PU components as the hybrid emulsions (Table II) were prepared by mixing of AC emulsion and PU dispersion sufficiently long to reach constant physical properties.

Preparation of AC-PU Hybrid Emulsions

A series of AC-PU hybrid emulsions with the AC component content shown in Table II were prepared. The preemulsion was made by dissolving emulsifier, Triton XN 45 S (1.5% on the total monomer) in water. The mixture of MMA and BA (1:1) and 0.15% of AA (based on the total weight of MMA and BA) were then slowly added under constant stirring to the emulsifier solution to form the preemulsion.

AC-PU hybrid emulsions (APE) were prepared by semibatch emulsion polymerization of AC monomers in presence of PU dispersion. The same reactor as for preparation of AC emulsion was charged with the amount of aqueous PU dispersion (particle size of 43.0 nm), 10% of separately prepared AC preemulsion and 10% of po-

Table II Composition of AC-PU Hybrid Emulsions

	PU	APE 1	APE 2	APE 3	APE 4	APE 5	APE 6	APE 7	AC
Acrylic (wt %)	0	20	40	50	60	70	80	90	100
PU dispersion (g)	/	600.0	500.0	400.0	400.0	400.0	300.0	150.0	/
MMA (g)	/	25.67	57.03	68.44	102.66	159.69	205.32	230.99	/
BA (g)	/	25.67	57.03	68.44	102.66	159.69	205.32	230.99	/
AA (g)	/	0.077	0.171	0.205	0.308	0.479	0.616	0.693	/
Solid content of final emulsion (%)	34.2	39.6	44.4	46.4	48.2	50.8	51.2	56.7	49.9

tassium persulfate initiator solution. Potassium persulfate presented 0.4%, based on total solids of AC component. The content was heated to 70°C. After 0.5 h the remaining initiator solution and AC preemulsion were fed in two separate streams at a constant flow rate for 4 h.

CHARACTERIZATION

Observation of Acrylate-PU Microphase Structure

Differential scanning calorimetry (DSC) was performed to characterize the thermal response properties of the coatings prepared from the AC-PU hybrid emulsions and physical blends. The samples were cured for 7 days at ambient conditions. They were then placed in a vacuum until a constant weight was obtained.

DSC was performed on a Perkin Elmer 7 calorimeter, with nitrogen purring the cell at the heating rate of 20°C/min from -120°C to 60°C. In order to investigate potential morphological changes during heating, a sample was quench cooled to -120°C and after 5 min reheated to 60°C.

Particle Size and Particle Size Distribution

The particle size and particle size distribution of AC-PU hybrid emulsions and blends were measured with photon correlation spectroscopy on a MALVERN ZETASIZER 3000. The measuring range of the apparatus was 3–3000 nm. The samples of the emulsions were diluted and directly placed in the capillary cell. The temperature of the cell was kept at approximately 25°C.

Observation of Emulsion Particles by Using Scanning Electron Microscope Microscopy

Scanning electron microscope (SEM) analysis was performed using JEOL T 300 emission SEM. The samples were imaged at 20 kV accelerating voltage and analyzed by the conventional secondary electron imaging technique. Highly diluted samples were coated with a thin layer of gold to reduce any charge build-up on the fracture surface.

Observation of the Molecular Mass and Molecular Mass Distribution by Gel Permeation Chromatography

The average molecular weights M_n and M_w were determined by gel permeation chromatography

(GPC) using Hewlett Packard HPLC 10/90 equipped with a refractive index detector. Two PLgel mixed-bed columns (10 μm and 5 μm) were used for the analysis. The latex samples were dissolved in *n*-Methyl pyrrolidone (NMP) and 0.01% LiBr was added. Each solution (25 μL) was injected into the NMP flow stream and pumped throughout the column at a flow rate of 0.5 mL/min. The average molecular weights were calculated from molecular weight versus retention time curves of monodisperse polystyrene standards.

Observation of the Minimum Film Formation Temperature

Minimum film formation temperature (MFFT) was performed using SHEEN MFFT Bar.60. The instrument consisted of a substrate plate with a temperature gradient. The film of the emulsion was cast on the plate and allowed to dry at the substrate temperature. After the film was dried it was visually inspected for formation damage such as cracks and other discontinuities. The lowest temperature at which a consistent and coherent film was formed was MFFT.

Determination of Rheological Properties

The rheological tests were performed under steady and oscillatory shear conditions at 25°C. Controlled stress rheometer Haake RheoStress RS 150, equipped with the double cone sensor system (DC 6/°4) was used. Rheological properties were studied under small and large deformations by applying different measuring procedures: stress and frequency sweeps, stress ramps, and multistep sequences.

Measurements of Mechanical Properties of Dried Films

The hardness of the films was measured by the Koenig method (DIN 53157). A film of the emulsion was cast on a glass plate and cured for 5 days at ambient temperature. An average of five measurements was taken to report.

Tensile properties, particularly tensile strength and elongation at break, were measured at 20°C using ZWICK 1435 tensile testing machine with a cross-head speed of 20 mm/min. The specimens of casted films were 15-mm wide and 50-mm long. An average of at least five measurements of each sample was taken for the report.

Table III Glass Transition Temperatures of AC-PU Blends

Sample	Composition AC/PU	Tg-Lower (°C)	Tg-Upper (°C)
PU	0/100	-58.2	
B1	20/80	-52.3	5.5
B2	40/60	-53.8	14.2
B3	50/50	-52.1	12.4
B4	60/40	-51.4	10.8
B5	70/30	-51.7	14.5
B6	80/20		14.3
B7	90/10		14.3
AC	100/0		19.5

RESULTS AND DISCUSSION

Observation of Microphase Structure

The microphase structure was investigated by DSC method. The shift of T_g was used as a measure of compatibility between polyacrylate and PU in AC-PU hybrid emulsions (APE). The values were compared with glass transition temperatures of physical blends of AC emulsion and PU dispersion. The experimental results are listed in Table III.

Pure PU dispersion and pure AC emulsion show very sharp glass transitions at -58.2 and 19.5°C , respectively.

Emulsions prepared with physical blending exhibit two distinct T_g 's, one of PU and one of acrylate component. The T_g 's are shifted with re-

spect to the pure polymers from 4.4 to 6.8°C at the lower temperature and 5 to 14°C at the upper temperature. The shifts are the result of partial compatibility and interdiffusion of PU and AC components and indicate some degree of miscibility. The blends with 80 and 90 wt % of AC emulsion show only one T_g at 14.3°C . It may be assumed that the influence of AC component in the mixture is predominant.

The APE emulsions exhibit only one broad glass transition. The T_g increases with the increasing amount of AC component and is almost the same as the T_g 's calculated by eq. (2) for three component systems (Fig. 1). The T_g values of pure AC components (MMA and BA) were taken from the literature.⁸ The appearance of a single T_g in hybrids means that they are homogenous at the molecular level. This molecular level mixing is demonstrated by broad glass transitions in the temperature range above 70°C as is indicative of entangled AC and PU chains, compared with larger individual AC- and PU-rich domains present in blends with two distinct T_g 's (Fig. 2).

Observation of Particle Morphology

Determination of the microstructure of emulsion particles was made by SEM and photon correlation spectroscopy. Hybrid emulsions were prepared by polymerizing a mixture of AC monomers in the presence of PU with the particle size (number average particle diameter) of 43.0 nm, which were used as seeds. The particle size dispersion index was defined as d_w/d_n ,⁸ where d_w and d_n are the weight and the number average of particle

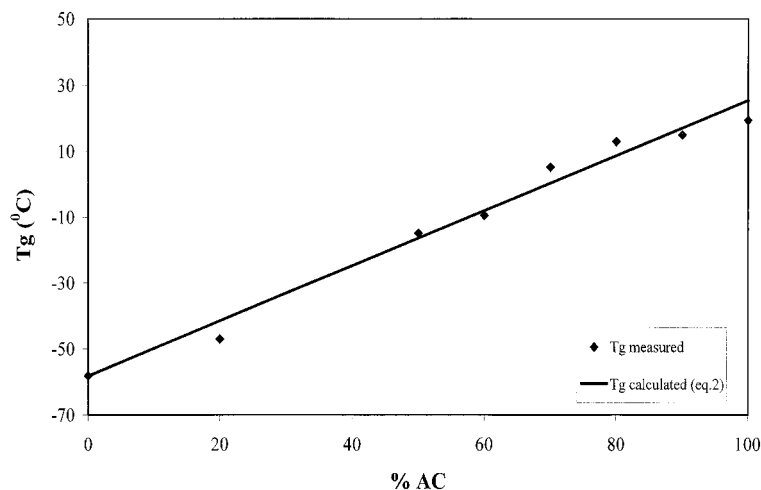


Figure 1 T_g dependence on weight fraction of acrylic component in acrylic polyurethane hybrid emulsions.

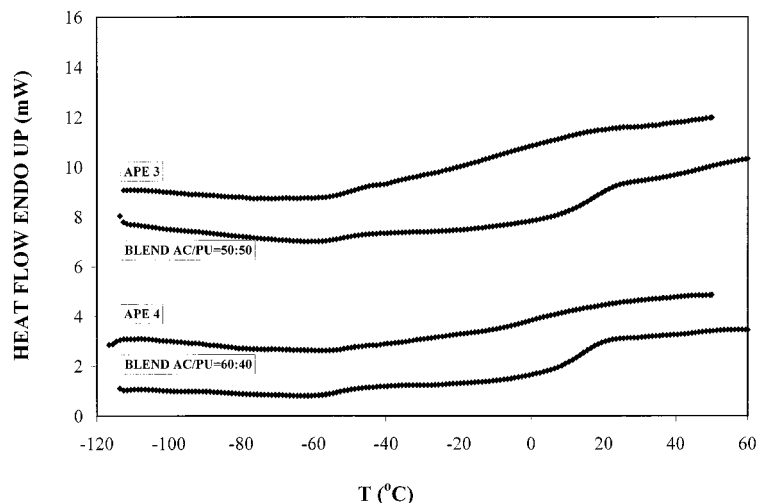


Figure 2 DSC curves of APE 3, APE 4, and physical blends with composition AC:PU=50:50 and 60:40.

size, respectively. The index for PU dispersion was 1.09. Only a small amount of emulsifier was used to stabilize the hybrid system by adsorption on the seed particles. Very narrow particle size distribution indicates poor secondary nucleation in hybrid emulsions. The average particle size of the prepared hybrid emulsions increases in non-linear manner (Fig. 3). Hybrid emulsion with 20 wt % of AC component has the same particle size as pure PU. With increasing AC/PU ratio to 40/60, the average particle diameter slightly increases from 43.0 to 56.2 nm. Further addition of the AC component results in a drastic increase of the average particle size. At AC/PU ratios from 50/50 to 90/10 the particle size becomes larger, due to the AC monomers tendency to swell into

the PU particles. This results in larger particle size after polymerization. It is also possible that when more AC component is introduced the fusion of particles further proceeds to form much larger particles.

AC-PU hybrid emulsions are monodispersed with narrow distribution of particle size. The particle size dispersion index is in the range from 1.00 (APE 3) to 1.06 (APE 6). The secondary nucleation is neglected and the higher amount of AC component is reflected in a linear relation between particle size and AC/PU ratios.

SEM pictures of hybrids show different particle morphologies such as hemisphere structure and sandwich-like structure (Fig. 4). This confirms that PU and AC components affect each other.

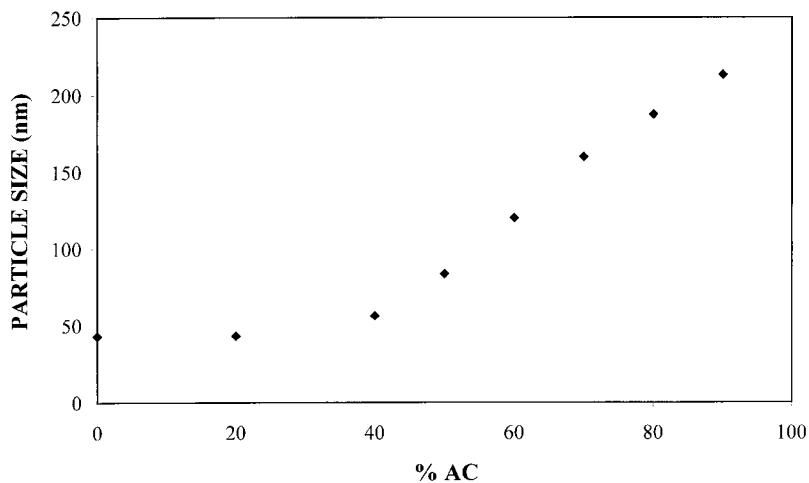


Figure 3 The particle size dependence on composition of acrylic polyurethane hybrid emulsions (the term particle size means number average particle diameter).

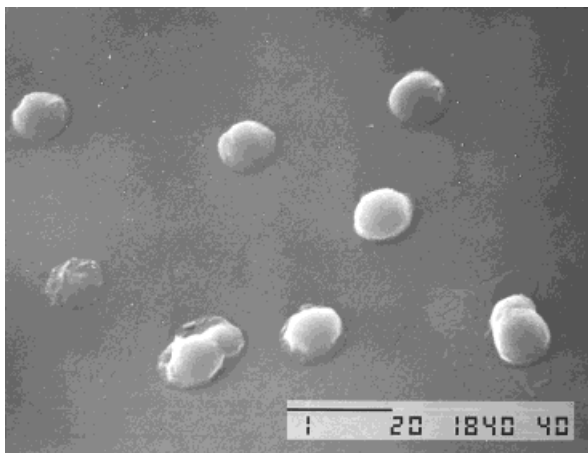


Figure 4 SEM photograph of acrylic polyurethane hybrid emulsion APE 7 presents different particle morphologies (the scale bar is 1 μm).

Emulsions prepared by physical blending of AC and PU in different proportions have the particle size in a range from 146.4–176.1 nm. Blends with weight percent of AC up to 50% show bimodal distribution of particle size. For example, a blend with composition AC/PU of 20/80 has half of the particles almost of the same size as PU dispersion, namely 44.8 nm. The rest of the particles are 169.8 nm in size (AC emulsion has the particle size 164.3 nm). The particle size dispersion index for this blend is 1.56. Blends with AC/PU ratios higher than 60/40 have almost uniform particle size in a range from 152.0 nm to 160.7 nm, which is comparable with the particle size of pure AC emulsion. This is probably the result of the predominant influence of larger AC particles.

Physical blends show in some cases bimodal distributions of particle size and also SEM photographs confirm the presence of particles which are only mixed together (Fig. 5).

Observation of Average Molecular Weights

Molecular weights were determined by using the polystyrene calibration curve. Therefore, the molecular weights are not absolute but relative to each other. The results are listed in Table IV.

AC emulsion shows bimodal distribution of molecular weights. Two main peaks can be observed from the chromatogram. The peaks at the retention times of 17.698 and 24.760 min indicate the M_w of 1.23×10^8 g/mol and 7.70×10^5 g/mol, respectively. Also evident is more than one small peak in the low-molecular-weight region. These peaks are the result of secondary interactions of

AC acid's hydroxyl groups with column packing. The total average molecular weight of AC is 2.55×10^7 g/mol.

PU dispersion has the average M_w of 2.16×10^6 g/mol. Molecular weight polydispersity index (PDI) defined as the ratio of M_w/M_n is 17.7. This value of PDI indicates some degree of branching between PU chains. Branching is also evident from the results of mechanical property measurements. PU dispersion has high Young's modulus resulting in a more rigid and less flexible film.

AC-PU hybrid emulsions show monomodal distribution of molecular weights, which slightly decrease with increasing AC/PU ratios (Table IV). The intermolecular bonding forces between the AC and the PU component cause a reduction in hydrodynamic volumes of macromolecular chains. The hydrogen bonding mechanism between urethane -NH- and acrylate carbonyls or -OH groups from AC acid were also detected with other measurements (DSC, testing of mechanical properties, and rheological behavior). The intermolecular interactions contract the hybrid polymer chain entanglements. This is shown in longer retention time and lower average molecular weights.

All physical blends, except from the one with AC/PU ratio 20/80, show bimodal distributions of molecular weights. The results of the M_w , M_n , and the PDI of the two separate peaks present in blends are listed in Table IV. The chromatogram of blend with 20 wt % of AC component shows only one peak with calculated M_w 2.72×10^6 g/mol. With increasing AC/PU ratio another peak

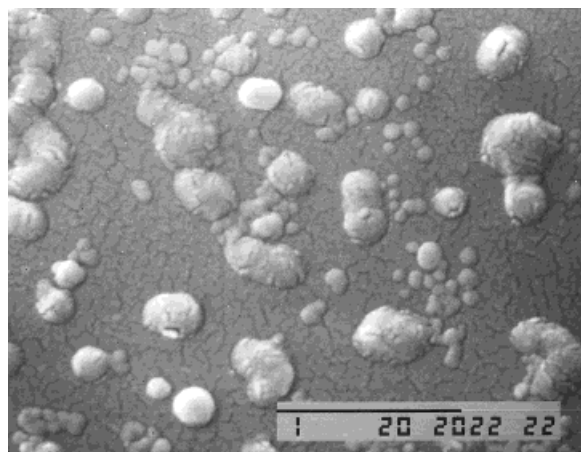


Figure 5 SEM photograph of acrylic polyurethane physical blend with composition AC: PU = 50:50 confirms the presence of larger AC and smaller PU particles (the scale bar is 1 μm).

Table IV Molecular Weights of AC-PU Hybrid Emulsions and Blends

Composition AC/PU	M_w^-		M_n^-		M_w^-		M_n^-		PDI-BLEND (Separate Peaks)	M_w^- BLEND ^b · 10 ⁻⁵ (g/mol)	M_n^- BLEND ^b · 10 ⁻⁵ (g/mol)	PDI- BLEND ^b
	APE · 10 ⁻⁵ (g/mol)	APE · 10 ⁻⁵ (g/mol)	APE · 10 ⁻⁵ (g/mol)	APE · 10 ⁻⁵ (g/mol)	(Separate Peaks)	(Separate Peaks)	(Separate Peaks)	(Separate Peaks)				
0/100	21.6	1.22	17.7	17.7	21.6	1.22	17.7	17.7	21.6	1.22	17.7	17.7
20/80	12.6	0.80	15.7	26.2	27.2	1.04	26.2	26.2	27.2	1.04	26.2	26.2
40/60	14.6	0.73	20.0	22.9 ^d	22.9 ^d	0.85 ^d	26.9 ^d	26.9 ^d	65.2	0.88	74.1	74.1
50/50	10.8	0.71	15.2	1410.6 ^c	1410.6 ^c	1076.84 ^c	1.3 ^c	1.3 ^c	78.4	0.82	95.6	95.6
60/40	10.3	0.66	15.6	21.7 ^d	21.7 ^d	0.78 ^d	27.8 ^d	27.8 ^d	123.5	0.85	145.3	145.3
70/30	9.1	0.54	16.8	1452.0 ^c	1452.0 ^c	1100.33 ^c	1.3 ^c	1.3 ^c	140.2	0.65	215.7	215.7
80/20	7.8	0.53	14.7	19.1 ^d	19.1 ^d	0.78 ^d	24.5 ^d	24.5 ^d	177.2	0.74	239.5	239.5
90/10	/	/	/	1307.2 ^c	1307.2 ^c	880.70 ^c	1.5 ^c	1.5 ^c	156.6	0.54	290.0	290.0
100/0	7.7	0.33	23.3	17.0 ^d	17.0 ^d	0.58 ^d	29.3 ^d	29.3 ^d	255.0	0.42	607.1	607.1
	1225.3	623.10	2.0	1263.0 ^c	1263.0 ^c	870.67 ^c	1.5 ^c	1.5 ^c				
				13.3 ^d	13.3 ^d	0.63 ^d	21.1 ^d	21.1 ^d				
				1217.7 ^c	1217.7 ^c	748.32 ^c	1.6 ^c	1.6 ^c				
				10.7 ^d	10.7 ^d	0.46 ^d	23.3 ^d	23.3 ^d				
				1112.2 ^c	1112.2 ^c	707.12 ^c	1.6 ^c	1.6 ^c				
				7.7 ^d	7.7 ^d	0.33 ^d	23.3 ^d	23.3 ^d				
				1225.3 ^c	1225.3 ^c	623.10 ^c	2.0 ^c	2.0 ^c				

^a PDI = M_w^-/M_n^- .^b M_w^- -blend, M_n^- -blend, and PDI-blend are the average M_w^- , M_n^- , and PDI values for the total, in some cases bimodal, distribution of molecular weights.^c First peak of the molecular weight distribution in bimodal blends.^d Second peak of the molecular weight distribution in bimodal blends.

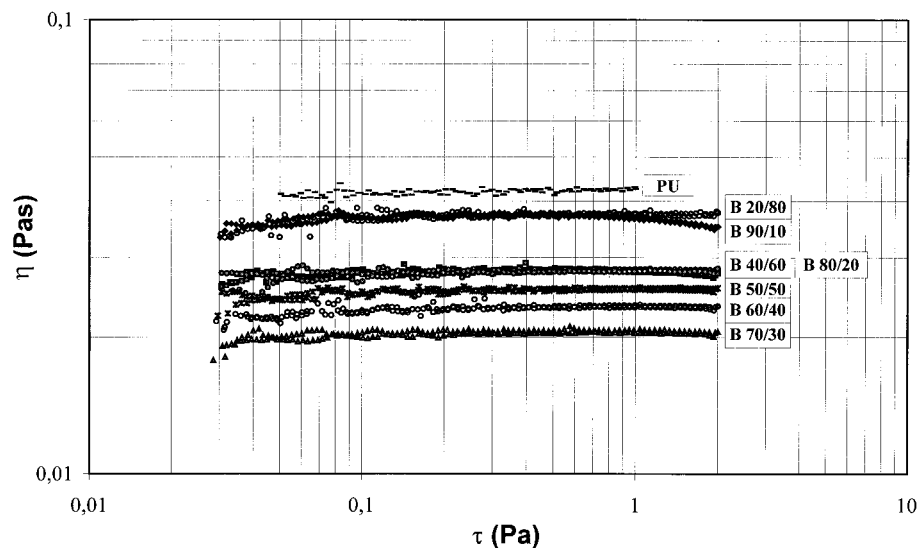


Figure 6 Flow curves of all physical blends (AC/PU) and PU dispersion.

in the higher molecular weight region become pronounced. The height and the area of these peaks (M_w ranges from 1.41×10^8 g/mol for B 2, to 1.11×10^8 g/mol for B 7) increase with AC concentrations in blends, due to influence of AC emulsion with bimodal distribution of molecular weights one M_w being 1.23×10^8 g/mol and the other 7.70×10^5 g/mol.

The total average molecular weights M_w and also the PDI of blends increase drastically with the percentage of the bimodal AC component with very high PDI of 607.1. All this confirms that AC and PU components are only mixed together.

Rheological Properties

PU dispersion shows Newtonian behavior ($\eta = 41.8$ mPas). The other basic component, AC emulsion, exhibits pseudoplastic flow properties with higher viscosity in the first Newtonian plateau ($\eta_0 = 235$ mPas).

Although the starting components show different rheological properties, the flow curves in Figure 6 demonstrate that all blends exhibited Newtonian behavior. In this case there wasn't probably any significant interaction between the particles. All blends of AC emulsion and PU dispersion are composed of particles of different sizes and size distributions, which results in lower viscosity values than for the two parent components. The measure of particle concentration is the particle volume fraction Φ , which is the single most important factor controlling the latex viscosity. It is calculated from the weight concentration of the

polymer solids and the density of polymer particles.⁹ The influence of physical mixing of AC emulsion and PU dispersion expressed by volume fraction of large particles (Φ_{AC}) on the relative viscosity (η_r) is shown in Figure 7. The relative viscosity (η_r) is expressed as the viscosity of the latex, divided by the viscosity of the aqueous phase.⁸ In blends of different particle sizes and size distributions small particles fit between the larger particles. The particle size distribution of blends examined was almost bimodal with the ratio of the diameters between larger AC and smaller PU particles around 3.82. The particle packing efficiency depends on the amount of larger with respect to smaller particles. The minimum viscosity was observed for the system containing 70 wt % of larger AC particles (at Φ_{AC} value of 0.77; Fig. 7).

The rheological properties of AC emulsion under nondestructive conditions of oscillatory flow showed predominant viscous contribution in the examined frequency range (0.1–1 Hz). Under the conditions of linear viscoelastic response determined by stress sweep tests, the system exhibits frequency independent dynamic viscosity and neglected elastic contribution.

AC-PU hybrid emulsions exhibit Newtonian behavior until the concentration of AC polymer in the AC/PU hybrids reaches 50/50. When the amount of AC polymer increases the Newtonian viscosity increases from 14.0 to 74.0 mPas. The molecular structure of these emulsions has no direct influence on the viscosity of the latex. For

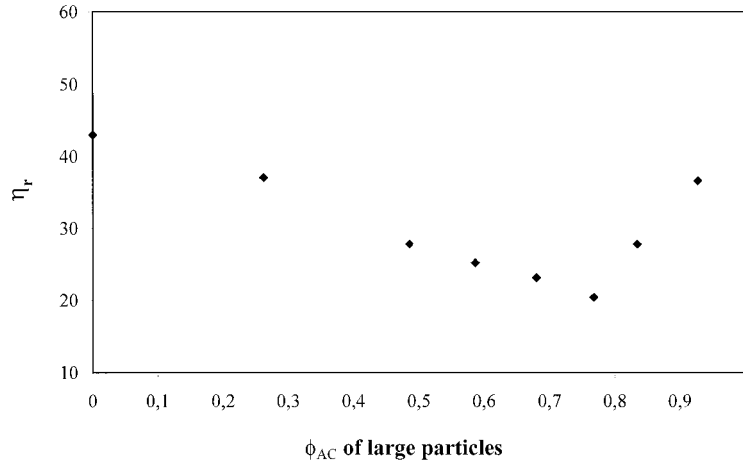


Figure 7 Relative viscosity of physical blends as a function of volume fraction (Φ_{AC}) of large particles (ratio of the diameter of large to small particles is 3.82).

these hybrid emulsions also the particle sizes are still small and the volume fractions are so low that no deviation from Newtonian behavior was observed. At higher AC concentrations ($> 60\%$) the AC-PU hybrid emulsions exhibit pseudoplastic flow properties and the viscosity of first Newtonian plateau drastically increases (η_0 ranges from 220.8 to 1345.1 mPas). When the amount of AC component is predominant, the emulsions exhibit nonmonotonous increase of viscosity η_0 . As

shown in Figure 8, the flow curves of APE 7 and APE 6 are appreciably higher than the rest of the curves. In this region of emulsion composition, solid volume fraction controls viscosity level. When relative viscosity of APE is plotted versus solid volume fraction (Fig. 9), relative viscosity asymptotically increases toward the limiting volume fraction (Φ_m), at approximately 0.56. These emulsions also have internal structures as a result of secondary intermolecular bonding forces,

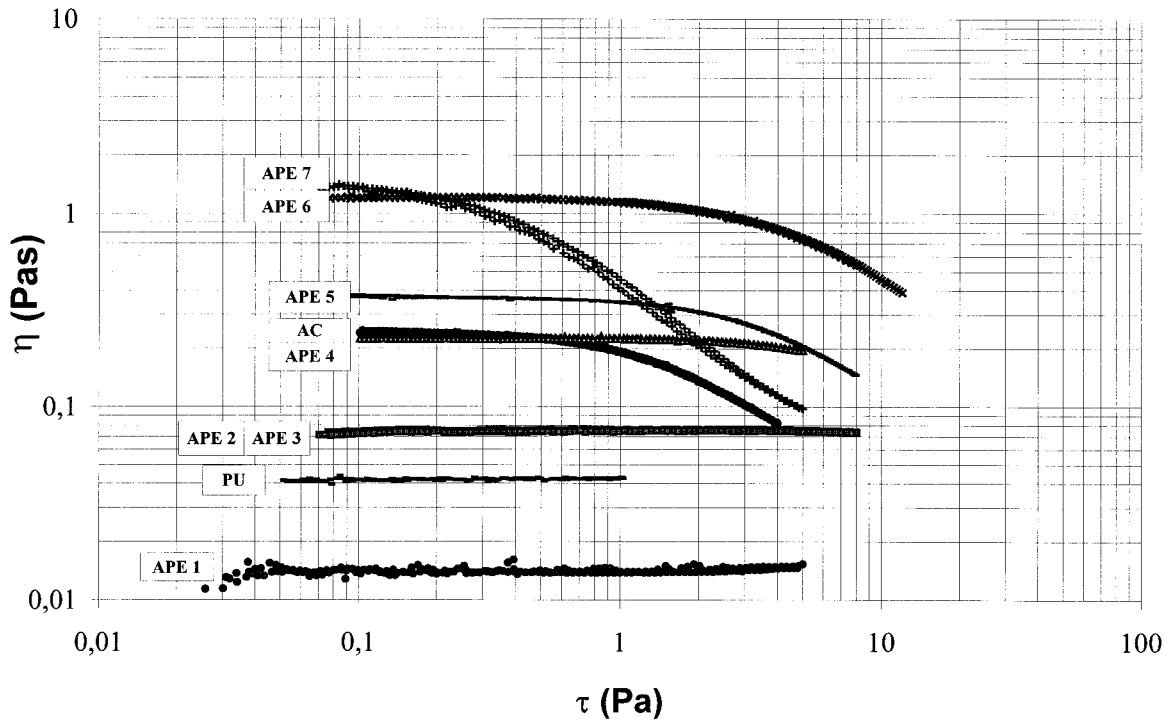


Figure 8 Flow curves of all acrylic polyurethane hybrid emulsions.

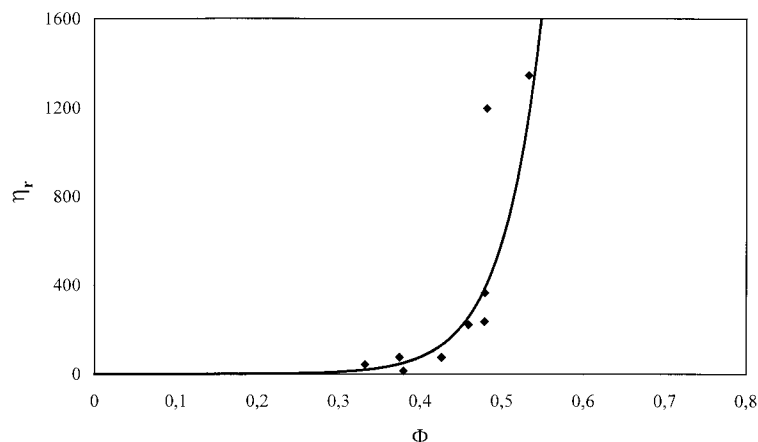


Figure 9 Relative viscosity of acrylic polyurethane hybrid emulsions as a function of volume fraction (the linear viscosity η_0 was taken for the pseudoplastic emulsions).

such as Van der Waals attractive forces, hydrogen bonding, Brownian motion, and electrostatic repulsive forces. The structural breakdown of this secondary network structure at higher shear rates leads to a decrease in viscosity and results in systems exhibiting pseudoplastic behavior.

The AC-PU hybrid emulsions at higher AC concentrations (> 60%) exhibit viscoelastic behavior under nondestructive conditions of oscillatory shear. The frequency sweep tests (0.1–2 Hz) were performed in a range of linear viscoelastic response. In the frequency range examined also these emulsions exhibit predominant viscous contribution. The highest elastic contribution of viscoelastic response is observed for the system APE 7, prepared with the highest solid volume fraction. Figure 10 illustrates the mechanical spectra of samples APE 5, APE 6, and APE 7. For

the system containing lower particle concentration (APE 5) the elastic contribution is almost negligible. The phase angle (δ) in this case remains close to 90° as shown in Figure 11. Increase of solids loading (APE 6 and APE 7) leads to particle interactions and appearance of elastic contribution in the frequency range examined. When frequency increases, the phase angle decreases and reaches the value of 54.7° for the system APE 7. The SEM photographs of these two emulsions show the presence of some nonspherical particles and aggregates as a result of secondary bonding forces. These are not close packed resulting in higher viscosity. The energy dissipated in breaking down the aggregates is reflected in a higher viscosity level, but the tendency of the aggregates to re-form imparts results in viscoelastic effect.

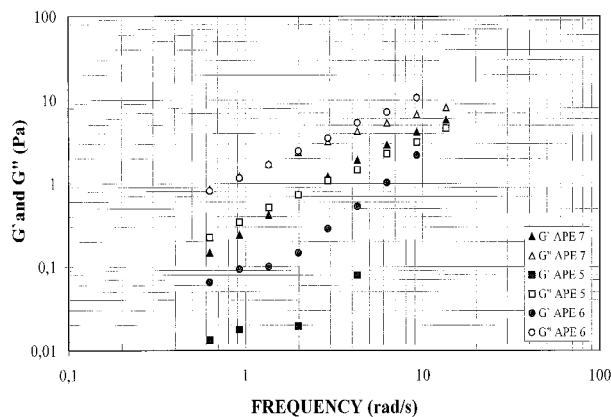


Figure 10 Loss and storage modulus of acrylic polyurethane hybrid emulsions as a function of frequency.

Mechanical Properties of Emulsion Films

The results of the measured mechanical properties are listed in Table V. Figure 12 shows the Koenig hardness as a function of composition for all AC-PU hybrid emulsions and blends. All hybrid emulsions show higher hardness values than blends. The lowest differences in hardness between hybrids and blends are obvious in emulsions with AC/PU varying from 60/40 to 90/10. The underlying reason is that the “soft” AC component diffuses across the interface of PU particles and causes the softening of the surface particle layer.

The tensile strengths of the hybrids, on the other hand, are well above the blends’ strengths and the value predicted by “the rule of mixtures” (Fig. 13).

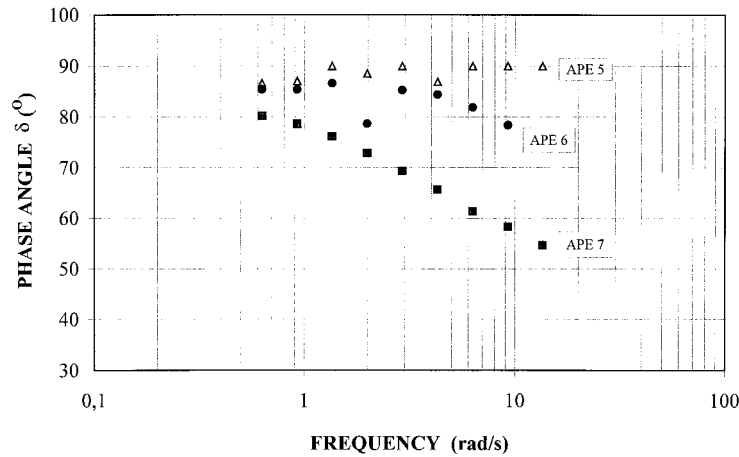


Figure 11 Phase angle δ dependence on frequency.

Physical blends show lower tensile strength perhaps because of the nonhomogeneity caused by separate regions of AC and PU components present in the film. The interfaces between these regions may have excessive internal stress and incomplete coalescence resulting in reduced cohesive film strength.

The elastic modulus decreases with increasing AC/PU ratio for both hybrid emulsions and blends (Table V).

Comparison of the results of mechanical properties between hybrids and blends indicates that hybrid polymers with higher compatibility between the AC and the PU component show pronounced characteristics of polyacrylate emulsions. The development of cohesive strength in hybrid emulsions results from particle/particle or interfacial contacts and molecular interdiffusion of polymer chains between the latex particles during the coalescence

phase in the film formation process. The final mechanical strengths of hybrid emulsion films increase as the particle boundaries disappear and critical degrees of entanglement of the interdiffusing polymer chains are achieved. In hybrid emulsions there are also small amounts of carboxyl groups incorporated into the latex particle structure, most likely at the surface of the particles. These groups are capable of associating with amine groups from PU through the hydrogen bonding mechanism. The interparticle interactions between these functional groups may result in an enhancement of the latex polymer film via an interfacial crosslinking mechanism.

CONCLUSIONS

In order to obtain cost/performance properties aqueous AC-PU hybrid emulsions were prepared

Table V Chemical and Mechanical Properties of AC-PU Hybrid Emulsions

	PU	APE 1	APE 2	APE 3	APE 4	APE 5	APE 6	APE 7	AC
Acrylic (wt %)	0	20	40	50	60	70	80	90	100
pH	9.51	8.06	8.04	7.52	7.64	7.34	7.01	6.11	9.05
MFFT (°C)	/	/	/	/	-5.1	-3.4	-2.0	-0.8	0.12
Tensile strength (N/mm ²)	20.7	20.7	17.6	12.3	14.8	10.0	10.2	9.0	3.7
Elongation at break (%)	5.9	46.3	144.7	160.3	245.2	262.1	295.1	319.7	340.6
Young's modulus (N/mm ²)	450.0	323.4	164.6	125.0	72.9	39.4	23.0	17.8	17.7
Koenig hardness (s)	129.2	92.6	59.7	51.2	34.8	24.9	20.6	19.1	12.1

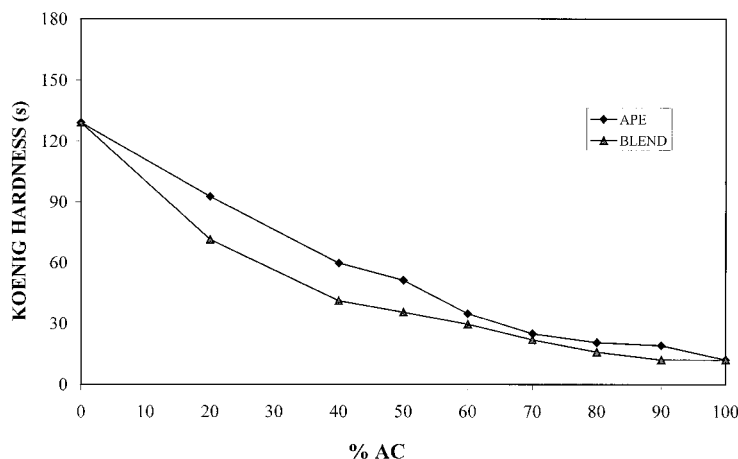


Figure 12 Koenig hardness as a function of composition of hybrid emulsions and blends.

by polymerization of a mixture of AC monomers (BA, MMA, and AA) in the presence of PU dispersion. The ratios AC to PU were varied from 0.25 to 9. A series of physical blends were also prepared using the same proportions of AC and PU components. The experimental results indicate an increase in the particle size of hybrids with a higher amount of AC incorporated in PU. This is caused by the AC monomers tending to swell into the PU particles. On the other hand, the blends show bimodal distribution of particle size in some cases.

The improved mechanical strengths of hybrids are the result of cohesive film formation via interdiffusion of polymer chains across the original boundaries. The separate regions of AC and PU components present in the dried film are assumed

to be the reason for the coarse mechanical properties of the blends.

The appearance of a single T_g indicates homogeneity of hybrid emulsions at the molecular level. Blends exhibit two distinct T_g 's shifted together, indicating a low degree of miscibility.

The differences between hybrids and blends are also obvious from the measurements of molecular weights. The blends show bimodal molecular weight distribution, whereas hybrids exhibit decreasing in M_w with increasing AC/PU ratios.

The results of rheological measurements indicate Newtonian behavior in all blends. The hybrids are Newtonian only at the weight fractions of AC from 0 to 0.5. At higher ratios, the hybrids are pseudoplastic indicating the presence of secondary bonding forces. APE 5, APE 6, and APE 7

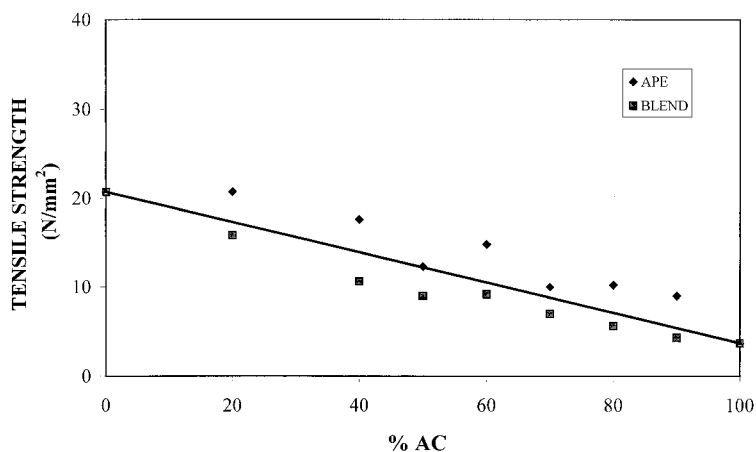


Figure 13 Tensile strength dependence on composition of hybrid emulsions and blends.

have δ values 86.6°, 78.4°, 54.7°, respectively, and show viscoelastic properties.

The experimental results indicate improved performance of AC-PU hybrid emulsions compared with the physical blends. By a careful selection of distinctive building blocks, the polymerization process and optimization of AC/PU ratios, tailor-made hybrid systems can be developed.

One of the authors (D. K.) wishes to thank MITOL d.d., Sežana for their support and financial assistance during the period in which this research was carried out.

The authors wish to acknowledge Mr. F. Barborič for GPC analysis, Dr. J. Stražišar for his active interest and advice on particle size measurements, Dr. M. Marinšek for SEM observations, and Mrs. P. Prosen for DSC analysis.

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