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Hybrid polymer latexes: acrylics–polyurethane from miniemulsion polymerization: properties of hybrid latexes versus blends

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Abstract

Hybrid polymer latexes polyurethane/polyacrylic esters, are prepared through miniemulsion polymerization of polyurethane solutions in acrylic monomers. The polyurethanes are prepared by condensation of isophorone diisocyanate on polypropylene glycol ($M_n = 1000$) and butane diol as chain extender. The NCO chain ends being reacted with water (which act as a further chain extender producing some urea bonds). They are miniemulsified in a mixture of methylmethacrylate and butylacrylate monomers, and the miniemulsion are polymerized using benzoylperoxide as initiator. Films were obtained for different hybrid latexes of various compositions. Their mechanical properties have been compared with those of films from the basic components (polyurethane and acrylic latexes), as well as films from blends of these components. Some specific features of the surface of these films are also discussed from microscope images (TEM and AFM) as well as from contact angle measurements.

Keywords: Hybrid latexes; Acrylic copolymers; Polyurethane

1. Introduction

A major objective in emulsion polymerization is to improve the properties of the binders used in the waterborne coatings, so as to fill the gap between these properties and those which can be obtained with the soluble binders which result in solvent-based coatings.

The most advanced materials produced upon emulsion polymerization are acrylic polymers containing a combination of several monomers. On the other hand, solvent based coatings are using a larger variety of polymers, some of them being produced through different polymerization mechanisms, such as polycondensation. Alkyd resins and polyurethanes belong to that category. They confer to the binders superior mechanical properties, in terms of flexibility and hardness. Then a lot of efforts have been devoted to introduce such components in waterborne coatings. The most common way to do that is the emulsification of solutions of these polycondensates. However, this process has many disadvantages, due to the fact that, after proper emulsification, the solvent has to be eliminated, most often through vaporization in the atmosphere, which is not a friendly environment operation. Further, there are limitation in the solubility of the given compounds in volatile solvents, and on the molecular weights compatible with that solubilization. Furthermore a rather big amount of surfactant is needed.

There is an obvious interest to combine in a same materials the properties of the two kinds of polymers. It is expected that the preparation of such hybrid materials should lead to improvements versus blends of acrylic latexes and emulsified polyurethanes.

The main purpose of the present paper is to compare the properties, and chiefly, the mechanical properties of the hybrid materials with their simple blended latexes; the materials are films from coalescence of the latexes.

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However, there have been not many reports in the open literature, about the preparation and the properties of these hybrid materials. The main usual route for such materials is to use a latex of modified polyurethane as seed for the preparation of an acrylic latex in a two step process. The first step is the preparation of the modified polyurethane from condensation of a diisocyanate with a mixture of a polyol and dimethylolpropanoic acid (DMPA). Then, after neutralization of the acid groups, the modified polyurethane is hydrophilic enough to be precipitated in water as stable particles. Several trials towards this objective have been described during the last decade. A paper by Hegedus et al. [1] did compare a set of so-called hybrid aqueous acrylic–polyurethane dispersions to the basic compounds and their blends, showing the interest of the hybrids. However, the preparation of these hybrids were not described, except for references to a few patents. The same year, Okamoto et al. [2] published a paper about blends of acrylic latexes and polyurethane dispersions. The acrylic latex is a copolymer of ethylhexylacrylate, methylmethacrylate, styrene and acrylic acid, with or without a ketone-containing monomer, diacetone acrylamide (DAAM). The polyurethane dispersion contains, adipic acid, dimethylolpropionic acid (DMPA) and an excess of diisocyanate. It is chain-extended either with a reactive hydrazine, or a nonreactive piperazine. Then, the two dispersions may or may not be crosslinked, through specific interactions of the keto-hydrazine chemistry. The crosslinking reaction is followed by FTIR. Although this reaction can be observed even at room temperature, the mixed dispersions displayed good storage stability without crosslinking. At variance, the crosslinked resulting films exhibited synergistic effects between the two polymers, including good solvent resistance, flexibility at low temperature, and good abrasion resistance. A similar approach with blends of modified crosslinkable systems was described in the field of alkyd resins [3].

The subject was further treated by a slovenian team, who carried out semi-batch emulsion copolymerization of acrylic monomers, from polyurethane seed particles. The polyurethane dispersions were commercial anionic polyester carbonate. In a first study [4], the authors did compare the hybrids resulting from the seeded emulsion copolymerization with blends of the polyurethane dispersion and acrylic latexes. It was shown that the improved compatibility of the hybrids causes improvements of both chemical and mechanical properties. However, the main interest of this team seems to be in the kinetics of the seeded emulsion polymerization [5], and the influence of the various parameters (concentrations, nature of the monomers) on both the kinetics and the mechanism of the process. They just mentioned that the final seeded hybrids do form structured particles.

Another interesting study was published by Zhang et al. [6]. The polyurethane was a polycondensate of toluene diisocyanate, polypropyleneglycol (PPG) and DMPA, the NCO end groups of which being reacted with hydroxypropylacrylate (HPA). They were used as seeds in the emulsion polymerization of MMA, initiated by KPS under soap-free conditions at 80 °C. The influence of the KPS and MMA concentration, and of the composition of the polyurethane (DMPA, HPA), on the kinetics, the particle size and the degree of crosslinking was studied. The mechanical properties of the cast films were strongly dependent on the composition of the seeds, the tensile strength being increased by the increase of both the DMPA and the HPA, at the expense of the elongation at break.

The most advanced approach published about this kind of hybrid materials was based on core-shell hybrid latexes [7]. Three different kinds of hybrid latexes were described, respectively, the A/U, the U/A and A/UgA type. In these products, a polurethane is produced first from an ethylacetate solution of polyester polyol reacted with isophorone diisocyanate which can be modified by DMPA. After neutralization of the acid, the solution is poured into a large amount of water, to cause a phase inversion and a dispersion; further addition of adipic dihydrazide was carried out before the elimination of the solvent. To the polymer containing dispersion are added the components of an acrylic copolymer, including diacetone acrylamide and polymerization is carried out (A/U type). The U/A type was obtained upon addition and polymerization in solution of the component of the acrylic copolymer containing a rather high amount of acrylic acid before emulsification and elimination of the solvent. For the A/UgA type, the polyurethane chains were end-caped with hydroxyethylmethacrylate before dispersion in water. Core shell morphology was obtained in the three cases, with a trend to have the modified polyurethane in the shell. Crosslinking was obtained from reaction of the hydrazide groups and the ketone groups, one of the component being added sometimes after the preparation of the latex, and then reacting during the formation of the film. Careful characterization of the film surface were done and the adhesive properties were measured showing improvements versus blends of latexes.

A second and more recent approach was published, using miniemulsion polymerization of a solution of polyurethane in acrylic monomers [8].This kind of approach has been previously used for hybrids of other kinds of polycondensates, such as alkyd resins [9], or polyesters [10]. With polyurethane, the product was modified by end-caping with an unsaturated linseed oil, with alkenyl double bonds of low reactivity. Some retardation of the polymerization was observed, and limited grafting of the acrylic copolymer on polyurethane took place, as well as a few percent crosslinking, but the majority of the double bonds were preserved for further curing reactions. It is interesting to note that the miniemulsion process has been used to prepare polyurethane from IPDI and a long chain alkyl diol [11], as well as other kinds of polycondensates. A recent review has been devoted to the use of the miniemulsion process for the preparation of many kinds of other hybrid materials [12].

In this paper, we have followed this second route with miniemulsion polymerization. The polyurethane was prepared from reaction of PPG with isophorone diisocyanate, butane diol being used as chain extender, and the monomers were a mixture of methylmethacrylate and butylacrylate. Some kinetic features of this miniemulsion polymerization have been already published [13].

Here the emphasis is put on the comparative properties of the hybrid latexes and the blends of their basic components, according to the composition of the acrylic mixture of monomers and to the amount of polyurethane.

2. Experimental

2.1. Materials

Polypropylene glycol 1000 (PPG-1000) supplied by Aldrich, was dried at 80 °C 0.1 mmHg for 4 h. 1,4-Butanediol (BDO) by Aldrich, was purified by vacuum distillation, isophorone diisocyanate (IPDI), dibutyltin dilaurate, methylmethacrylate (MMA), butylacrylate (BA), hexadecane (HD), benzoyl peroxide (BPO), were supplied by Aldrich, were used as received. Sodium dodecyl sulfate (SDS), supplied by Acros was used without further purification.

2.2. Polyurethane synthesis

A 1000 ml, 4-neek-flask separable glass reactor with mechanical stirrer, thermometer, condenser and nitrogen purge was used. Reaction was carried out in a N_2 atmosphere in a constant-temperature water bath. IPDI and dibutyltin dilaurate were first charged into the reactor and heated to 50 °C under stirring, PPG was then dropped into the reactor while keeping the temperature at 80 °C. The reaction proceeded over approximately 2 h, BDO was subsequently charged and reaction proceeded for another 4 h at 70 °C, upon obtaining the theoretical NCO/OH value of 1.2. The mixture was cooled to 50 °C. After dissolution in ethylacetate, end capping was carried out upon reaction of the solution at 60 °C with methanol to produce a reference compound (PU18D). Otherwise the crude product was dipped in water, where it precipitates in fine particles soft enough to produce films (PU18H). These products are further described in Table 1.

2.3. Miniemulsification of monomer solutions

Miniemulsion were prepared according to the recipes reported in Table 2: the desired amount of SDS was dissolved in about 300 g of deionized water. The BPO organophilic initiator was dissolved in the solution of PU18H in the monomer mixture of MMA and BA. Then the oil phase was added to the SDS solution and sheared for 12 min (1000 rpm). The pre-emulsion was sonicated for 10 min at 95% output with Branson ultrasonifier. In the cases of purely acrylic latexes, the PU18H was replaced with hexadecane.

2.4. Polymerisations

Immediately after sonication, the monomer miniemulsion was transferred to a 1000 ml, equipped with a turbine stirrer, a thermometer and a reflux condenser. The system was purged for 15 min with nitrogen and brought to the polymerization temperature (75 °C). Approximately, 30 g of sample were taken at intervals during polymerization. The overall monomer conversion was determined by gravimetry from these samples. The data of average monomer particle size were obtained from the dynamic light scattering method, while the molecular weight measurements were carried out using size exclusion chromatography (SEC). Waters instrument and polystyrene standards to calibrate the elution volume scale.

2.5. Polymer characterization

Differential scanning calorimetry (DSC) has been carried out, using a Perkin-Elmer Pyris 1 instrument. Films were prepared from dry casting at 20 °C in a flat Teflon capsule so as to obtain a 0.75 mm homogeneous film.

Dynamic mechanical analysis (DMA) measurements were performed in a torsion mode with an inverted pendulum. The measurements were carried out at a fixed frequency (0.1 Hz) from −50 to 50 °C with a heating rate of 1 K/min. The imposed deformation was about 10^{-4}, which ascertains that the measurements were in the linear viscoelastic region. Samples dimensions were around $10\times2\times0.75\ \mathrm{mm}^3$. The set-up provides the storage and the loss components of the complex shear modulus (G' and G'', respectively) and the ratio of these two components $\tan\delta = G''/G'$.

The tensile tests were performed at ambient temperature using an Instron 8150 machine at constant cross-lead rate fixed at 50 mm/min. Samples were dumbell-shaped with typical dimensions of 2 mm width and 15 mm length. Nominal strain ε_n and nominal stress σ_n are given by the relationships: $\varepsilon_n = (L - L_o)/L_o$ and $\sigma_n = F/S_o$ where F is the

Table 1
Molecular weights of the polyurethanes

Run	IPDI/PPG	BDO	NCO/OH	End cap	M_n	M_w/M_n
3–1.2	3	1.5	1.2	OMe	6000	2.2
3–1.2	3	1.5	1.2	W	11,100	5.4

Table 2
Recipe of PA and PU18H-acrylate hybrid minieumlsion polymerization

Miniemulsion	Ingredients (g)						
	PU	MMA	BA	H_2O	SDS	BPO	HD
PA10	0	50.0	50.0	300	1.0	0.5	2.0
PA11	0	60.0	40.0	300	1.0	0.5	2.0
PUA84	22.0	44.0	29.6	300	2.5	0.5	0
PUA88	36.0	36.0	24.0	300	2.5	0.5	0
PUA99	22.0	37.0	37.0	300	2.5	0.5	0
PUA17	36.0	36.0	24.0	300	2.5	0.5	0

applied force, L is the sample length during the test (L_o at $t=o$) and S_o the initial cross section. In the assumption of constant volume, true stress can be deduced from nominal data by $\varepsilon = \ln(\lambda) = \ln(\lambda + \varepsilon_n)$ where $\lambda = L/L_o$ is the stretching ratio and $\sigma = F/S = (1+\varepsilon_n)\sigma_n$.

The morphology of the films containing polystyrene was studied using TEM after staining the styrene units with uranylacetate solutions while AFM microscopy was carried out on purely acrylic materials and their blends or hybrid latexes with polyurethane. All the samples were imaged with a PicoSPM AFM from Molecular Imaging (Arizona) operating in the tapping mode and allowing phase imaging. All images were obtained in air at room temperature using silicon cantilever (OTESPA, Olympus, Japan, resonant frequencies around 300 KHz) and scanning frequencies around 1 Hz to minimize the signal/noise ratio.

Finally, contact angle measurements have been carried out using a Digidrop instrument with three different liquid probes: water, formamide and bromonaphtalene. The data were analyzed in the framework of the van Oss acido-basic approach based on the two crucial assumptions [14].

(i) The splitting of the total surface free energy into two components that contribute ‘independently’ to the total interaction:

$$\gamma^{\text{total}} = \gamma^{\text{lw}} + \gamma^{\text{ab}}$$

constituted of a long range interaction one γ^{lw} (Lifschitz–Van der Waals interactions) and a more short range acid–base one γ^{ab} originating from donor–acceptor interaction (Lewis acid–base).

(ii) The antisymmetric nature of the acceptor–donor interaction:

$$\gamma^{\text{ab}} = 2(\gamma^{+}\gamma^{-})^{1/2}$$

were γ^{+} and γ^{-} are the acceptor and donor surface tension components, respectively.

This last relation required that the liquid acceptor (donor) surface tension component be in interaction only with the solid donor (acceptor) and vice versa. If both terms, donor and acceptor, are negligible, the material is considered apolar; if one of the component is appreciable, the material is monopolar, and is bipolar when both components have to be considered.

3. Results and discussion

3.1. Polyurethane synthesis

When the PU, after chain extension with BDO, are dipped into water and not end-caped through reaction with an alcohol, its molecular weight is increased, as shown in Table 1. Before dipping it remains residual NCO groups able to react with water with elimination of CO_2 and formation of a NH_2 end group. If this reaction is not immediate and completed, these new end groups can react further with other residual NCO groups, leading to urea bond and further chain extension, so explaining the quasi two times increase of M_n between the two first lines of Table 1. In addition the polymolecularity index also increases by a factor of more than 2, the extent of the side reaction depending on the local conditions of concentration of NCO and NH_2 groups.

The reference compound end caped through reaction with methanol (first line of Table 1) was not used to prepare the hybrid miniemulsions and materials.

3.2. Acrylic latexes

A few latexes of acrylics copolymers have been also prepared from miniemulsion polymerization of mixtures of acrylic monomers (and in some cases styrene), using hexadecane as costabilizer instead of polyurethane Their characteristics are reported in Table 3.

They are either copolymers of MMA and BA with two different compositions (50/50 or 60/40) or a terpolymer with 30% of styrene, in order to make possible the staining of the TEM images of the films. As discussed in our previous paper [13] some composition drift may occur during the synthesis of the latex, because the miniemulsion polymerization involves a batch process, and that the monomers have slightly different reactivity in radical copolymerization. Most probably, this composition drift is at the origin of the observed DSC diagrams showing two T_g. In addition the molecular weight of these copolymers are quite high and

Table 3
Characterization of pure acrylic latexes

Latex (%)	MMA (%)	BA (%)	ST (%)	M_n	M_w/M_n	T_{gA} (°C)		T_{gB} (°C)	
						T_{gi}	T_{gf}	T_{gi}	T_{gf}
PA10	50	50	0	740,000	2.7	−5.2	2.9	28	39
PA11	60	40	0	608,000	1.8	−6	13	24	44
PA12	20	50	30	203,000	2.5	−4	12.7	–	–

then the mobility of the macromolecules inside the polymer particles should be limited. This lack of mobility is not in favor of the homogeneity of the materials. This fact may be a second explanation of the appearance of two T_g.

3.3. Preparation and characterization of the hybrid latexes

The preparation of the hybrid latexes is carried out from polymerization of the miniemulsions of the solutions of the PU18H in a mixture of monomers, containing an oil-soluble initiator (see Table 2). Then the miniemulsions are stabilized against Ostwald ripening by the PU acting as the hydrophobe. In these polymerizations the monomer conversion was followed by gravimetry of the whole copolymer formed from samples taken at different times. The sampling procedure also allows to follow the evolution of the particle size. Typical results are shown in Fig. 1.

One can see that the polymerization is completed in a reasonable time, and that the size does not change very much all along the conversion from the size of the initial droplets to the final latex. So it can be concluded that the PU acts as a quite good hydrophobe to stabilize the droplets against Ostwald ripening and then the polymer particles.

An example of the evolution of the molecular weight distribution is reported in Fig. 2 from the initial PU18H to the final latex at high monomer conversion.

The final molecular weight distribution is clearly bimodal with a high molecular weight becoming more and more important as the conversion increases; this peak (B) is believed to correspond to a high M_w copolymer, which could have been formed through the conventional emulsion polymerization process of the same mixture of acrylic monomers. Such a feature might be expected, because the recipe does not include any transfer agent. The second peak (A) of smaller molecular weight is not very different from the initial SEC diagram of the PU. It is believed that it might result from some grafting process to the PU, most probably through a transfer reaction onto the NH groups of the PU polymer. This hypothesis has not been checked as we did not have a spectroscopic (for instance, an IR) detector for the SEC analysis. It must be noted that the molecular weight distribution is not always bimodal, as shown in Fig. 3 where one can see the case of a simply very broad distribution (for instance, PUA84). We believe that this possible bimodal character of the molecular weight distribution shows that the degree of grafting of the acrylic copolymer onto the polyurethane is rather limited, due to the fact that there are no reasons for the PU to participate in the polymerization process of the acrylic monomers, except for occasional transfer to the PU polymer. The extent of this transfer process is believed to be responsible for the broadness of the molecular weight distribution. No effort has been made to determine the extent of the possible grafting process, for instance, through selective extraction and fractionation procedures.

More data about the products of the hybrid latexes from the PU are reported in Table 4. It can be seen here that the molecular weight distribution is not always bimodal but remains quite broad. On the other hand, the DSC traces are sometimes displaying two transition where the contribution of the acrylic materials seems to be dominating. In fact, the second T_g observed when the amount of PU is 60% is a minor feature in the DSC diagram, and then can be practically neglected.

3.4. Morphology of films by microscopy

Films from these latexes, and also from the initial PU were prepared at room temperature or slightly higher (35 °C in case of acrylic copolymers with 60 MMA and 40 BA). A rapid analysis of a few films has been carried out by TEM and AFM microscopy. In order to improve the contrast of

Table 4
Miniemulsion polymerization results for latexes using PU18H precursor

PU name (%)	Precursor (%)	MMA (%)	BA (%)	Conv. (%)	D_n (nm)	SEC data				T_g	
						Peak B		Peak A		T_gA (°C)	T_gB (°C)
						M_n	M_w/M_n	M_n	M_w/M_n		
PUA84	30	60	40	99	148	133,000	9.1	–	–	13	
PUA88	60	60	40	93	183	383,000	2.7	3600	2	7	90
PUA99	30	50	50	96	150	–	–	–	–	0	–
PUA17	60	50	50	89	196	9700	69	–	–	0	30

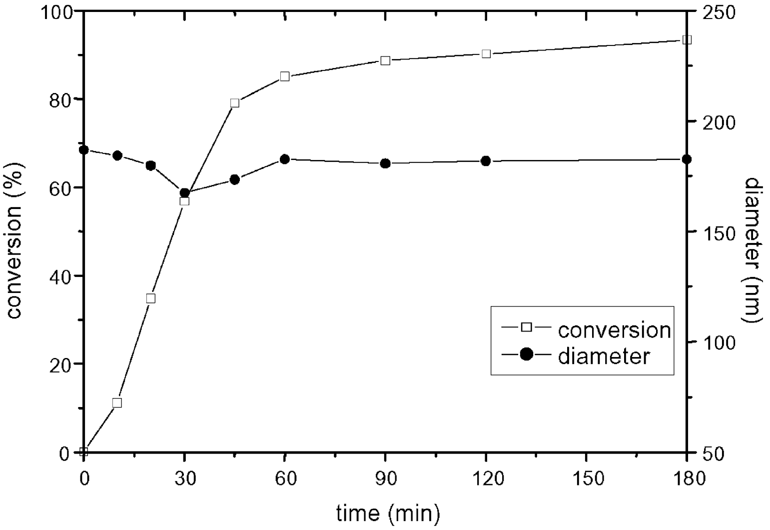

Fig. 1. Average particle size and total monomer conversion as a function of time for PUA88 miniemulsion polymerization at 75 °C, with BPO as initiator.

TEM images, the acrylic latexes have been modified by replacing a part of the MMA with styrene, because it is possible to stain the styrene-containing polymer with uranyl acetate. Examples of TEM images of blends of PU and acrylic latexes are shown in Figs. 4 and 5.

It can be seen that the picture is quite different according to the PU contents of the materials. Phase separation is much more pronounced when the PU contents is above 50%. One should expect that phase separation will be less important in the case of hybrid polymers as clearly evidenced further down through AFM pictures. Indeed, beside the fact that staining is not always possible, we have undertaken such kind of experiments because AFM imaging is done in air at room temperature and without any staining reflecting then more precisely the surface morphology and the organization of the latex films under normal operating conditions. Furthermore, the possibility to probe some how a visco-elastic contrast via phase imaging will help to gauge the efficiency of the miniemulsion polymerization approach.

Fig. 6 shows the surface morphology of a typical blend (AB4). It is readily visible (left) that a phase separation occurred for such 60% PU blend. The continuous binder matrix appeared smooth compared with the spheric-like structure of the acrylic latex inclusions. The stiffness contrast appearing in the phase image (Fig. 6 left) as black and white zones confirms that the presence of two distinct phases, the softer PU and the harder acrylate matrix, in agreement with the two tan δ peaks seen in the DMA trace in Fig. 7.

Before analyzing the hybrid latexes, it is interesting to note that both the bare components exhibit homogeneous AFM pictures if one take the precaution to clean up the

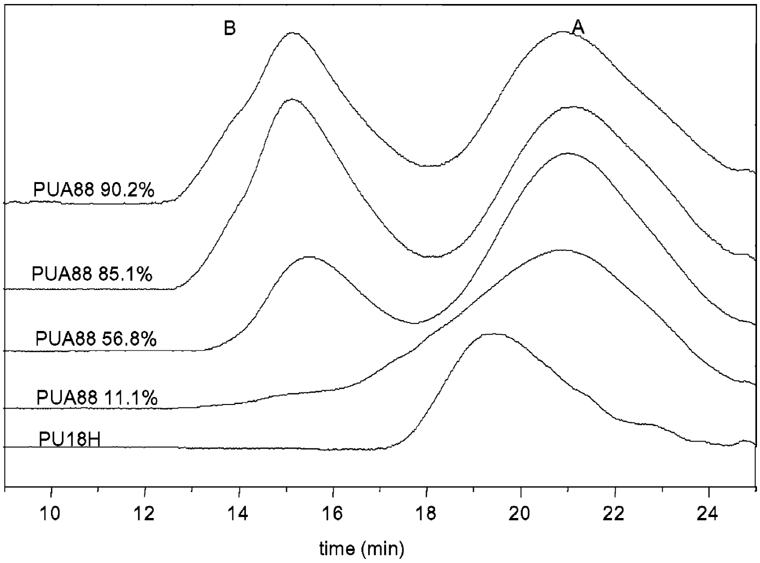

Fig. 2. SEC of PUA88(PU 3-1.2W:60/MMA:60, BA:40) at different conversions.

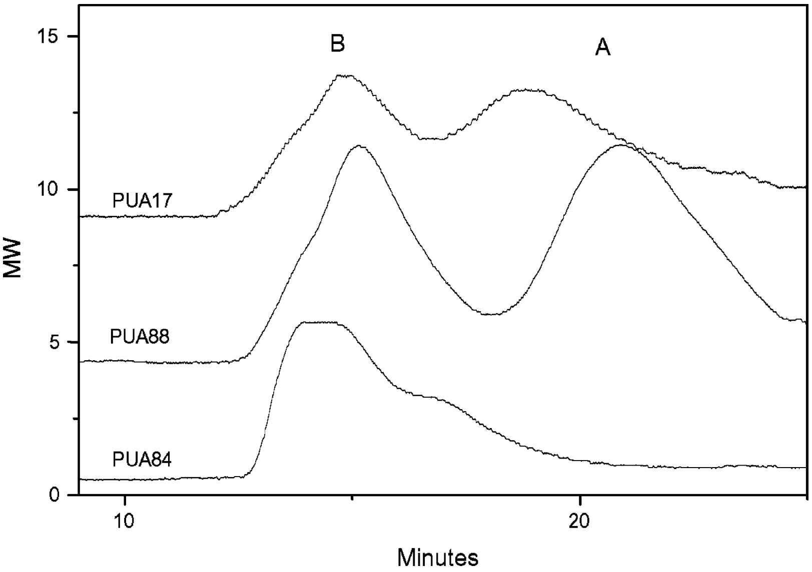

Fig. 3. SEC chromatogrammes of three final hybrid latexes from PU 3-1.2W. Their composition are: PUA17(60PU/MMA50/BA 50), PUA84(30/60/40) and PUA88(60/60/40).

surface, likely covered with the different surfactants used in the emulsion process. Fig. 8 shows such possible artifact in the case of an acrylic film, when it is not washed with water.

The Fig. 9 shows the rather smooth surface of a film from a typical hybrid latex (PUA 88) where the typical biphase organisation of the blend has disappeared. Furthermore, the phase image (right) does not reveal any appreciable 'mechanical' or 'visco-elastic' contrast. The compatibilized blend appears then homogeneous as confirmed by the single tan δ peak observed in DMA (Fig. 7).

In order to complement the study of the surface morphology of the different films, a physico-chemical analysis of these surfaces was carried out from contact angle measurements. The results using three different test liquids having unlike acido-basic nature are reported in Table 5.

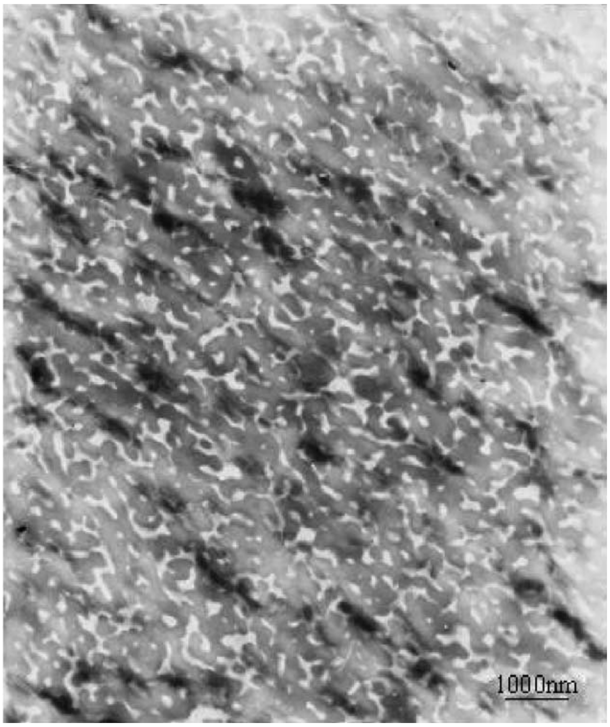

Fig. 4. TEM micrograph of the latex film obtained from the latex blend of PU and polyacrylate (Sty/MMA/BA 30/30/40) at 30/100 (W/W).

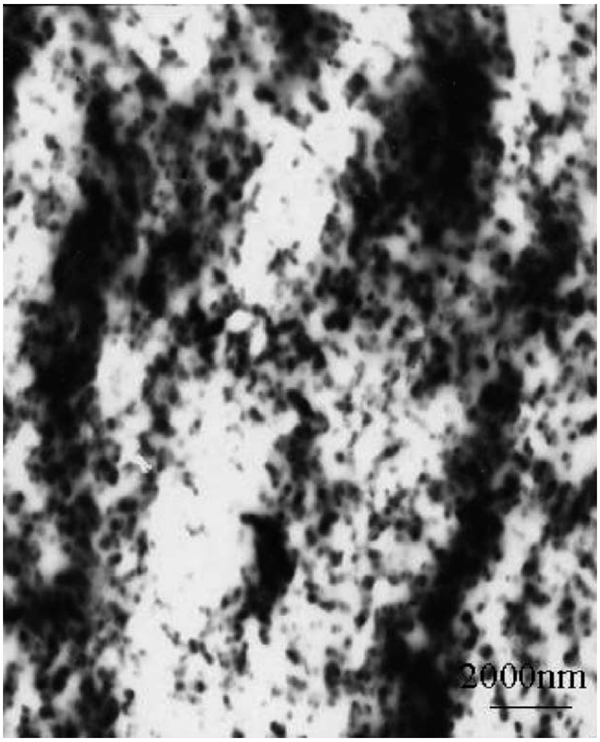

Fig. 5. TEM micrograph of the latex film obtained from the latex blend of PU and polyacrylate (Sty/MMA/BA 30/30/40) at 60/100 (W/W).

From these data it is possible, following the Van Oss approach to come back to the surface energy of the films. Fig. 10 shows the different contributions to the total surface free energy of the films prepared using the different acrylic and hybrid latexes. Different surface features can be retrieved from Fig. 10. In the case of bare latexes, the dispersive component contribute mainly to the total free energy according to the MMA (or BA) contents in the case of acrylic copolymer. The softer BA groups have, as expected, a higher impact on the surface energy even in the case of small amount difference between MMA and BA (PA10 versus PA11).

The average free energy of the blends are found in between the values of both the bare latexes as thought for films constituted of two low energy components. Furthermore, for a given polymer (either PA11 or PA10), the surface energy increases with the PU quantity. It should be noted nevertheless that, compared to the bare latexes, the acido-basic (or polar) contribution is lowered significantly in this case, except for AB4. Indeed, when dealing with blends with rubbery or soft chains, it is possible to minimize the surface free energy (and then the polar contribution) when air is the adjacent medium through surface reorganizations. In the case of AB4 however, where the MMA contents is the highest, reorganizations are minimized due to an higher T_g of the MMA groups leading to a strongest acido-basic contribution.

In the case of the hybrids the different components are somehow intimately compatibilized and cannot play their own role anymore as in the blends. It is expected that only the softer component will be responsible for the surface features. Indeed, the lowest surface energy is observed for the hybrid with the highest BA contents (PUA 99) and increases with the PU contents. The hybrid with the highest surface energy (PUA 88) has the lowest BA and the highest PU contents, and the strongest modulus (see further down). Both the low energy contribution and the ability to minimize the surface free energy through re-orientations (low T_g) confer to the BA groups a key role when dealing with top surface properties.

3.5. Mechanical properties

The mechanical properties of these films have been studied from stress–strain curves. The basic components PU and acrylic latexes were analyzed first, as shown in Fig. 11.

As expected, the films from latexes containing 50–50% of BA and MMA units (PA10) are softer than those with 40% BA and 60% MMA (PA11) with higher glass transition temperatures. The PA11 sample shows a yield point at very low elongation with a stress peak, then a minimum in the curve followed by a strain hardening phenomenon. The maximum stress (near the yield point) is close to 10 MPa and the elongation at break is about 400%. PA10 film displays a pseudo-rubbery behavior, and no distinct yield point can be observed. However, it may be interesting to compare the stress level at the elongation corresponding to the yield point. We have measured the stress value when the slope of the stress–strain curve strongly decreases (called yield stress in the following). For PA10 the yield stress is lower than for PA11 (around 2 MPa) but the strain at break is increased above 500%. The presence of consequent strain hardening and large value of strain at break indicate that these film are probably slightly crosslinked, owing to a transfer reaction onto the butylacrylate units of the copolymer [15]. This can also be at the origin of a second

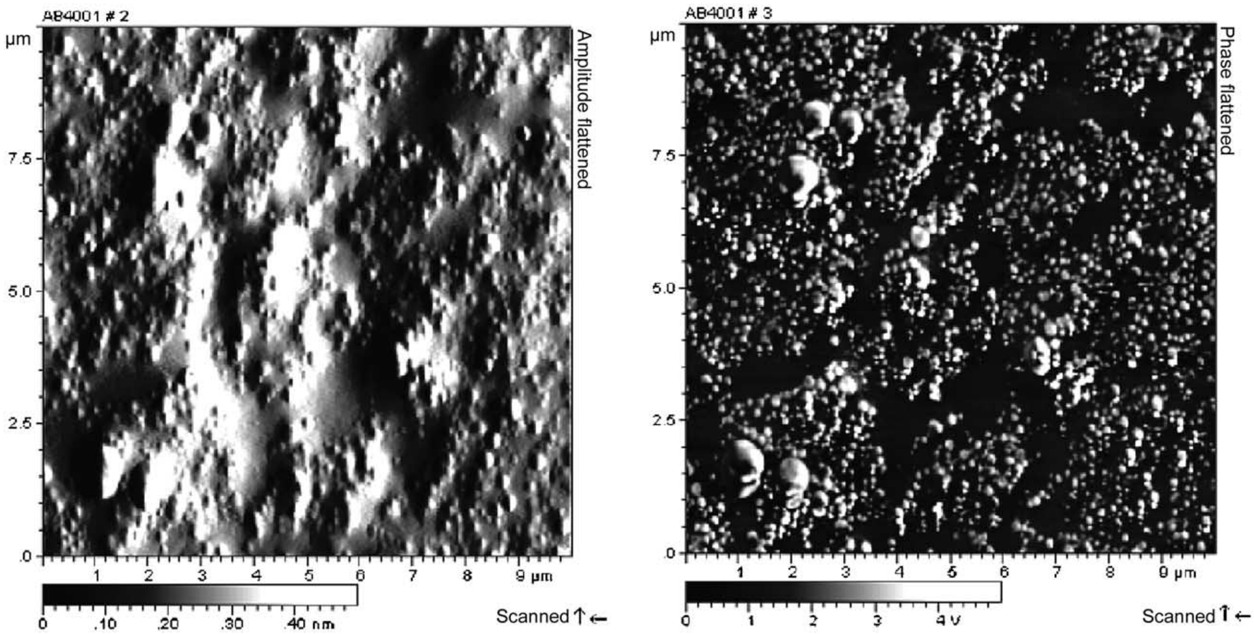

Fig. 6. Topographic (left) and phase (right) AFM images of the AB4 blend: 60 PU18H/60 MMA/40BA.

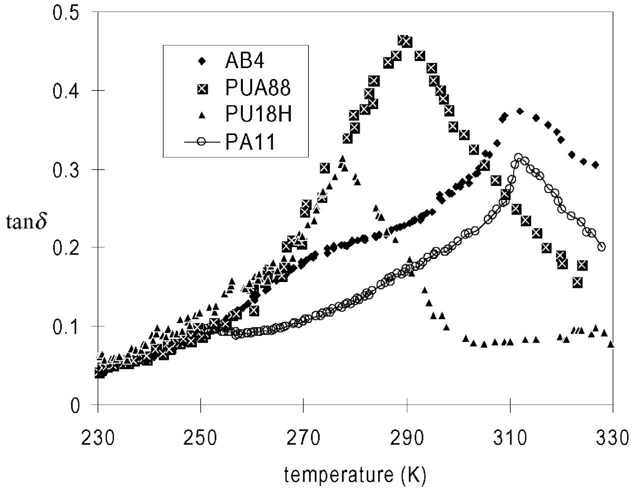

Fig. 7. Dynamic mechanical analysis of the components PU 3A-1.2, PA11 their mixture AB4, and the hybrid latex with PU/MMA/BA of 60/60/40.

T_g, although this feature might also be due to a composition drift caused by a difference of reactivity between the two monomers. More surprisingly the film from PU18H also shows a rubbery behavior; however, it is well known that the polyurethane chain is a succession of hard and soft segments; the elastomeric behavior might then be likely due to some phenomenon of physical crosslinking [16].

Four blends of the basic compounds have been studied, containing either 30 or 60 parts of PU, and 100 parts of either PA10 or PA11. The results are shown in Fig. 12.

First, we can compare the sample in terms of the acrylic monomer composition. It can be observed that the smallest values of the yield stress are obtained for the PAB1 and PAB2 samples, i.e. when the blends are composed with the copolymer containing equal amounts of BA and MMA units. The influence of the PU contents can be discussed comparing either PAB1 and PAB2, or PAB3 and PAB4. In the case of the softer acrylic latex (PAB1 and PAB2), the sample containing the higher PU content, i.e. PAB2, displays a slightly higher yield stress and also a much higher strain at break. However, the influence of the PU contents is less pronounced with the blends containing the harder acrylic latex (PAB3 and PAB4) in the case of lower PU contents (PAB3), the presence of a yield point and the plastic behavior seen for PA11 is observed. All these results are consistent with the morphology studies, and indicate that the acrylic phase acts as a continuous matrix with soft inclusions.

Fig. 13 displays the stress–strain curves for the corresponding hybrids, with either 30 or 60 parts of PU with 100 parts of either 50–50 or 60–40 MMA-BA copolymer. We can once again compare samples in terms of the amount of PU and the composition of the acrylic copolymer. Whatever the composition of the acrylic phase, the higher amount of PU leads to lower yield stress (compare PUA88 versus PUA 84 and PUA17 versus PUA99). At a given PU contents, the softer acrylic latex leads to lower yield stress (compare PUA 99 to PUA 84 and PUA17 to PUA88). The most important information is the comparison of blends versus hybrids. As compared to the blends, in the case of a PU contents of 30 parts, the improvement of hybrids versus blends is clearly demonstrated as it can be seen in Fig. 14.

The hybrid samples shows an higher yield stress and a larger strain at break. This can be an effect of the

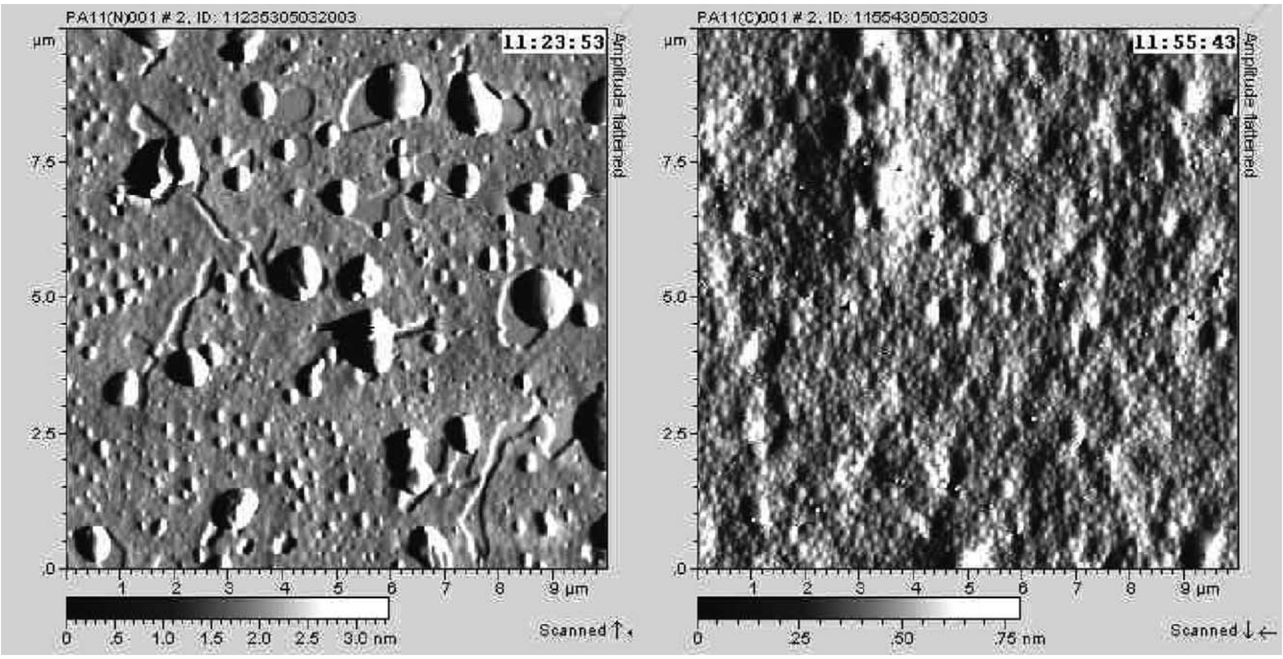

Fig. 8. Topographic AFM images of the acrylic latex (50MMA/50BA) PA11 before and after cleaning the film with pure water. The bumps seen in the left image are likely due to aggregated surfactant.

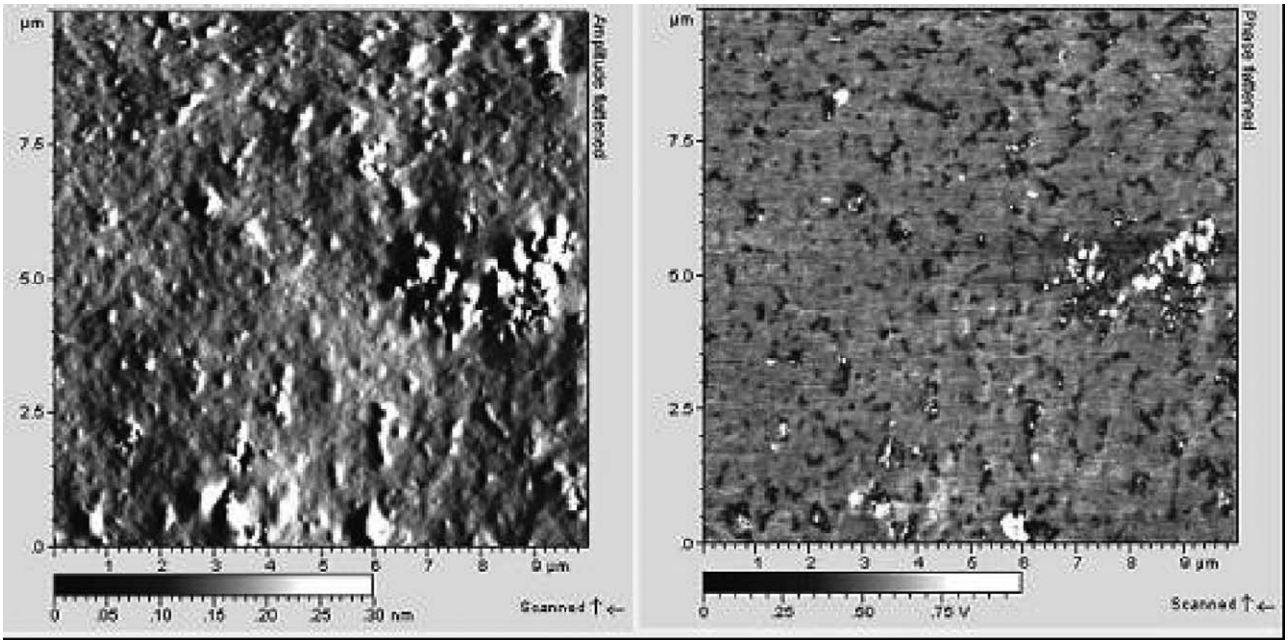

Fig. 9. Topographic and phase AFM images of an hybrid latex (PUA 88).

co-continuous morphology. However, in the case of the samples with 60 parts of PU, the improvement is not so evident. This last point indicates that there is an optimum in the composition of the hybrid (PU versus acrylic amounts).

4. Conclusion

A variety of hybrid latexes, combination of polyurethane, from isophorone diisocyanate and polypropylene glycol, and acrylic MMA/BA copolymers, have been prepared through miniemulsion polymerization of solution of polyurethane in mixture of acrylic monomers. The blends of the basic components have been prepared as well. Films have been obtained from either the basic components (including PU) or their blends and finally from the hybrid latexes. Surface morphology and wetting properties of these films have been carried out through TEM and AFM microscopy, and contact angle measurements, respectively. The mechanical properties of these films were also measured from either stress–elongation curves or DMA analysis. It can be concluded that the films from the hybrid latexes are much more homogeneous than the corresponding blends with the same overall composition. There is evidence for phase separation in the blends, chiefly when the PU contents is high. On the other hand, all the materials exhibit rubbery properties. The better homogeneity of the hybrids, as compared to the blends, leads to improved and tunable mechanical and surface properties according to the composition of the hybrid. However, it appears that, at

Table 5
Contact angles of films of the different materials: basic, blends and hybrids with three test liquids: water, formamide and bromo-2naphtalene

Materials	Composition			Contact angle with		
	PU (%)	MMA (%)	BA (%)	Water	Formamide	Bromo-2naphtalene
PU18H	100			68.9	61.5	44.5
PU not wash	100			59.4	37.9	62.3
PA11	0	60	40	66.8	67.8	41.4
PA11 not W	0	60	40	32.4	59.1	29.7
PA10	0	50	50	85.6	85.1	64.6
AB1	30	50	50	75.5	63.6	44.4
AB2	60	50	50	63	64.1	53.5
AB3	30	60	40	67.9	59	35.3
AB4	60	60	40	71	50.2	55
PUA84	30	60	40	73.4	52.4	26.9
PUA88	60	60	40	66	67.8	34.3
PUA99	30	50	50	81.4	62.7	53.4
PUA17	60	50	50	81.9	64.7	45.7

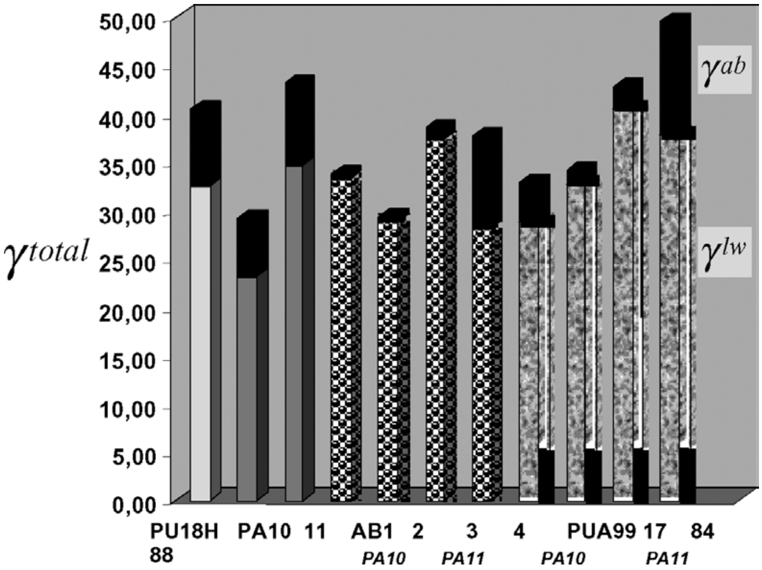

Fig. 10. Dispersive γ^{lw} and acido-basic γ^{ab} surface energy contributions to the overall surface free energy γ_{total} for bare acrylic, blend with PU and hybrid latexes.

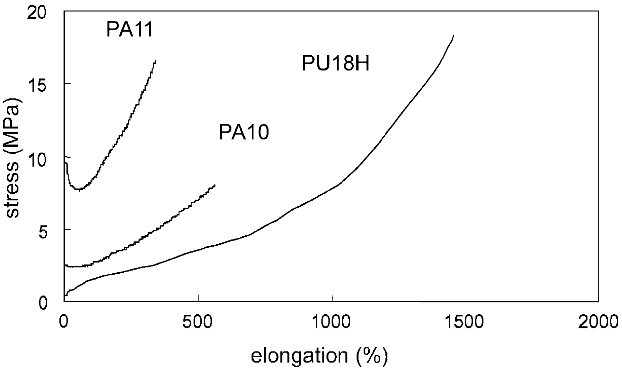

Fig. 11. Stress–elongation curves for the three basic components of the blends.

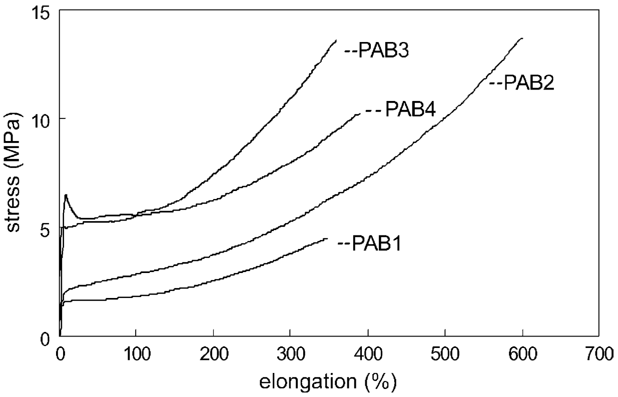

Fig. 12. Strain–stress curves for the blends of the basic components. PAB1: blend of 30PU and 100 PA10; PAB2: blend of 60PU and 100 PA10; PAB3: blend of 30PU and 100 PA11; PAB3: blend of 60PU and 100 PA11.

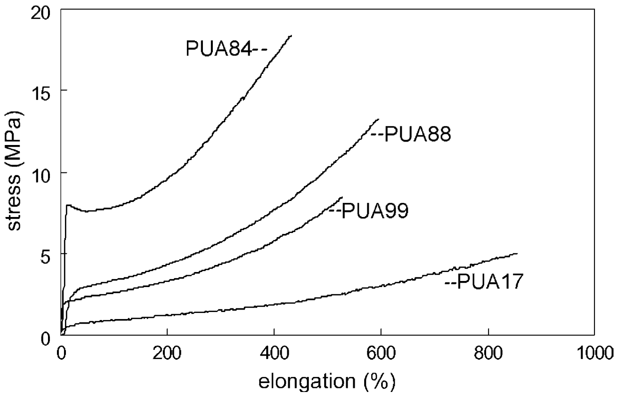

Fig. 13. Strain–stress curves for polyurethane–acrylate hybrid polymer with different monomer weight ratio (PU/MMA/BA): PUA84 (30/60/40); PUA88 (60/60/40): PUA99 (30/50/50); PUA17 (60/50/50).

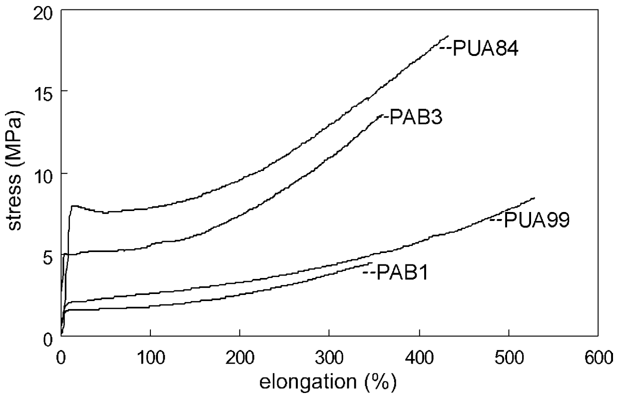

Fig. 14. Comparative stress–elongation curves for blends and hybrids containing 30 parts of PU. (PAB1 and PUA 84, PAB3 and PUA 99).

least in terms of PU contents, there is probably an optimal composition, because the improvement observed for the mechanical properties is more visible when the PU contents is 30% than when it is 60%.

A possible further improvement of the homogeneity of the hybrids from miniemulsion polymerization should be to use PU end-caped with a reactive acrylic group, able to participate in the radical polymerization process. Such an approach has been followed in our laboratory and will be published [17].

It should be interesting to compare the properties of the two classes of hybrid latexes, respectively, from seeded emulsion polymerization and from miniemulsion polymerization. Such comparison will be the subject of our future work.

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