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Structure and properties of polyurethane/polyacrylate latex interpenetrating networks hybrid emulsions

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Abstract Some new kinds of novel polyurethane (PU)/polyacrylate (PA) latex interpenetrating networks (LIPNs) were synthesized. Firstly PU dispersions were synthesized by self-emulsification polymerization. Then PU/PA LIPNs using PU dispersion as the seed were prepared by soap free emulsion polymerization. The effects of different PU/PA ratios, the blending method and the NCO/OH molar ratio of PU components on PU/PA LIPNs performance were also investigated. The structure and properties of PU/PA LIPNs such as mechanical properties, particle size, morphology of the surface were characterized by dynamic mechanical analysis, scanning electron microscopy, and dynamic light scattering. It was found that

PU/PA LIPNs can markedly improve the water resistance and the mechanical properties of PU latex much more than those of PU/PA physical blends due to a great deal of interpenetrating and entangling between PU and PA latex. Moreover, the particle size of PU/PA LIPNs is related to the PA content and NCO/OH molar ratio of PU components: the higher the NCO/OH molar ratio in PU dispersions, the larger is the particle size of PU/PA LIPNs, and the average particle size of PU/PA LIPNs becomes larger with an increase in PA content.

Keywords Polyurethane · Polyacrylate · LIPN · Emulsion polymerization

Introduction

Interest in waterborne emulsion polymerization has increased in recent years since more stringent environmental laws are expected in the future. Waterborne polymers have become an important class of materials in the paint and ink industry. Generally waterborne polyurethane (PU) and polyacrylate (PA) resins are important kinds of waterborne polymers and have a wide range of applications such as adhesive and coating materials. However, both of them are inferior to the corresponding solvent-based counterparts because of hydrophilic groups or surfactants which are introduced to impart a dispersion stability in aqueous media to these resins [1, 2, 3, 4, 5].

Progress in new polymer synthesis techniques makes it possible to modify the performance of waterborne emulsions compared with solvent-borne coatings. Known polymerization methods include the formation of an interpenetrating network or seeded emulsion polymerization. Interpenetrating polymer networks (IPNs) are intimate mixtures of crosslinked polymers held together by permanent entanglement [6]. They are classified as latex IPN (LIPN), sequential IPN (SIPN) and simultaneous IPN (SIN). Because of their in processability and environmental advantages, LIPNs have been extensively investigated in the recent years [7, 8, 9, 10]. LIPN is usually prepared via a two-stage emulsion polymerization technique and a variety of complicated factors are involved in the synthetic process such as solubility parameters,

interfacial tension and crosslink density of multipolymer [8]. The kinetic mechanism and controlled morphology of the resulting LIPN are still unexplored.

In an attempt to gain deeper insight into the structure and properties of PU/PA LIPN hybrid emulsions, we first prepared PU dispersions, followed by using PU dispersion as the seed to prepare PU/PA LIPN emulsions under a soap free emulsion polymerization technique. The structure and properties of these hybrid emulsions are characterized by dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and dynamic light scattering (DLS).

Experimental

Material

N220 polyether diol (hydroxyl number 56 mgKOH/g, Jinlin Petrochemical Co.) and dimethylol propionic acid (DMPA) were dried and dehydrated at 105 °C under vacuum. Methyl acrylate (MA), butyl acrylate (BA) and methylacrylic acid were distilled again under a nitrogen atmosphere prior to polymerization. Toluene-2,4-diisocyanate (TDI), triethylamine (TEA), ethylenediamine (EDA), *N,N* dimethylformamide (DMF), potassium persulfate ($K_2S_2O_8$) and de-ionized water were all analytical grade purity and used as received.

Preparation of PU/PA LIPN emulsions

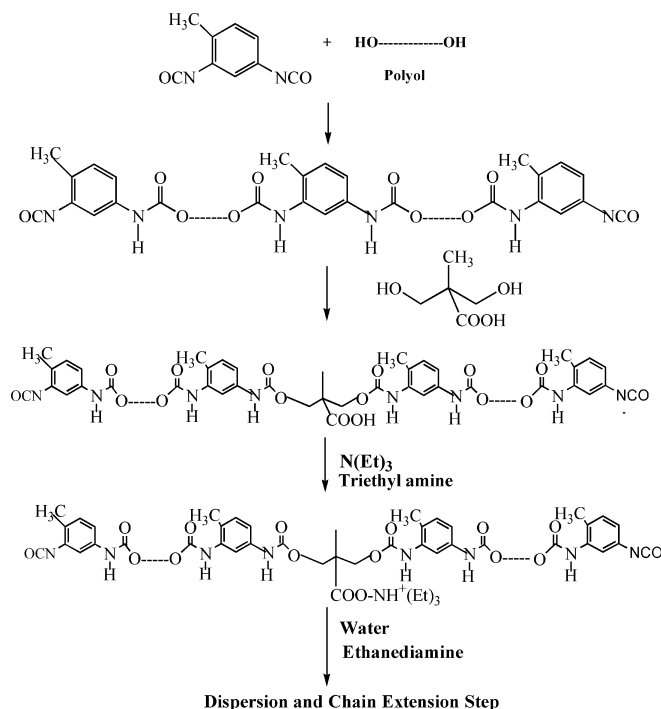
Preparation of PU dispersions

PU dispersions were prepared by a self-emulsification method. A polyaddition reaction was conducted in a 500-ml four-necked flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen gas inlet. Polyether diol and DMPA were dried and dehydrated at 105 °C under vacuum for 2 h, and the system was cooled to 85 °C. TDI and the catalyst were added to the mixture in an oil bath for 3 h. DMF was added to this system in order to reduce the viscosity, then the reaction temperature was lowered to 50 °C and the mixture stirred continuously for 3 h. The prepolymer was then chain extended and neutralized by adding TEA and EDA respectively. The PU dispersions with a solid content of 20 wt% was obtained by adding a calculated amount of deionized water to the mixture solution. The synthetic route is shown in Scheme 1.

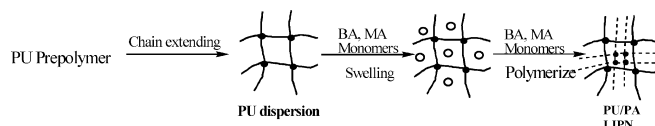
Preparation of PU/PA LIPNs

PU/PA LIPNs prepared with PU dispersions as the seed The preparation of PU/PA LIPNs was carried out by using soap free polymerization, which used PU dispersions as the seed emulsions. We prepared several LIPNs of different PU/PA ratio. For example, when the weight ratio of PU/PA LIPN was 1:1, 105 g PU dispersion seed (20%) and 84 g deionized water were introduced into the four-neck flask along with 0.084 g $K_2S_2O_8$ initiator and heated to 60 °C. Then 8 g MA and 13 g BA monomers were dropped into the mixture for 2 h at 80 °C and it was heated to 85 °C and reacted for 2 h. A schematic diagram of the synthesis of LIPN is shown in Scheme 2.

Physical polymer blends between PU dispersions and PA emulsions In order to compare PU/PA LIPNs with physical PU/PA blends, physical blends were prepared by mixing PU dispersions with PA emulsions at different PU/PA ratios. The effects



Scheme 1 Synthetic reaction of PU dispersion



Scheme 2 Schematic diagram of synthesis of PU/PA LIPN

of different PU/PA ratio on the properties of their blends were also investigated.

Film formation

Films for the tests were prepared by casting emulsions onto a Teflon plate, followed by drying for 1 week at ambient temperature (~23 °C). The thickness of the dried films was about 0.5 mm.

Characterization

Water absorption

Dried films (30 mm×30 mm; original weight designated as W_0) were immersed in water for 24 h at 23 °C. After the residual water had been wiped from the films using filter paper, the weight (W_1) was measured immediately [11].

The water absorption was calculated as follows:

$$\text{Water absorption } R (\%) = \frac{W_1 - W_0}{W_0} \times 100\%$$

Scanning electron microscopy (SEM) The morphology of the surface of PU/PA LIPN was observed by SEM (JSM-5900, Japan Electron Co.). The LIPN films were frozen under liquid nitrogen and mounted on a stub using gold paint. Subsequently, they were

coated with gold (100 Å) in a Balzers SCD 004 sputter coater. The instrument was operated at 20 kV, and the magnification employed was 10,000 $\times$.

Dynamic mechanical analysis (DMA) The viscoelastic properties and miscibility of PU/PA LIPNs were characterized by DMA (DMA 2980, TA Instrument). All measurements were at 1 Hz, over the temperature range from -100 to 100°C with a heating rate of approximately $3^{\circ}\text{C}/\text{min}$.

Particle size and distribution of PU/PAA LIPNs The emulsion particle sizes of emulsions were measured by using DLS (IETASIZER 3000HSA, Malvern Instruments). The samples of emulsions were diluted with deionized water to adjust the solid content to around 1 wt% and directly placed in the cell. The temperature of the cell was kept at around 25°C and the measuring time was 300 s.

Results and discussion

Water resistance

Table 1 shows that the water absorption of PU dispersion, PU/PA physical blend (PU/PA ratio, wt/wt = 1/1) and PU/PA LIPN (PU/PA ratio, wt/wt = 1/1) is 141.1%, 52.32% and 37.71% respectively. Using the methods of physical blending and LIPN, the water resistance of PU dispersions can be increased markedly by blending with PA emulsions. Moreover the water resistance of PU/PA LIPN is better than that of PU/PA physical blends.

Mechanical properties of the hybrid emulsions

Effects of different blending ways on mechanical properties of emulsions

Table 2 shows that the tensile strength of PU/PA LIPNs (PU/PA ratio, wt/wt = 1/1) and PU/PA physical blends emulsions (PU/PA ratio, wt/wt = 1/1) is 6.67 MPa and 3.35 MPa respectively, the elongation at break of PU/PA LIPNs (PU/PA ratio, wt/wt = 1/1) and PU/PA physical blends emulsions (PU/PA ratio, wt/wt = 1/1) is 758% and 345% respectively. This indicates that the mechanical properties of PU/PA LIPNs are twice as good as those of PU/PA physical blends. This is because a great deal of interpenetration and entanglement may improve compatibility between hybrid emulsions significantly.

Effect of PA content of PU/PA LIPN on mechanical properties

The effect of PA content of PU/PA LIPNs on mechanical properties is shown in Figs. 1 and 2. With the increase of PA content from 20 to 33%, the tensile

Table 1 Water resistance of PU/PA LIPNs

Sample	PU:PA weight ratio	Water absorption R (%)
PU emulsion	1:0	141.20
PU/PA physical blending	1:1	52.32
PU/PA LIPN	1:1	37.71

Table 2 Effects of blending method on mechanical properties of PU/PA LIPNs

PU:PA weight ratio	Blending method	Tensile strength (MPa)	Elongation (%)
1:1	Physical blending	3.35	345
1:1	PU/PA LIPN	6.67	758

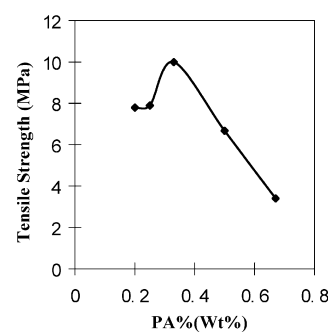


Fig. 1 Effects of PA contents of PU/PA LIPNs on their tensile strength

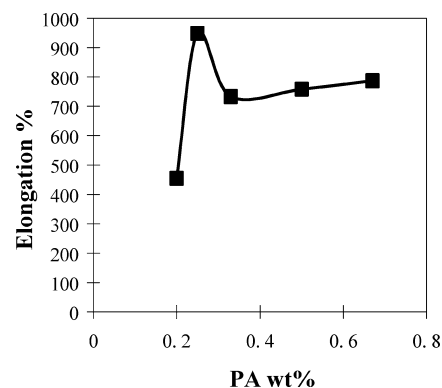


Fig. 2 Effects of PA contents of PU/PA LIPNs on their elongation

strength of PU/PA LIPN increases from 7.63 to 9.99 MPa, then the tensile strength of PU/PA LIPN decreased markedly with further increase of PA content. The tensile strength of PU/PA LIPN presents a maximum value at 33% PA content, while the elongation of PU/PA LIPN at break has a maximum value at 25% PA content. This is because with lower PA content, a great

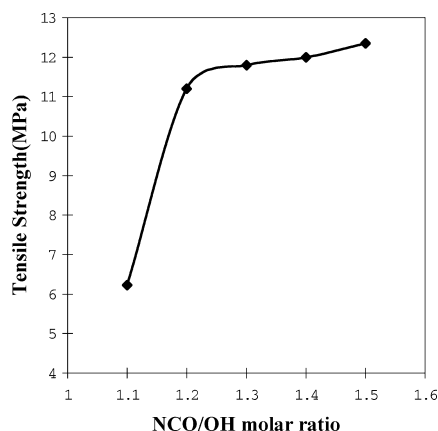


Fig. 3 Effects of NCO/OH molar ratio of PU dispersions on tensile strength of PU/PA LIPNs

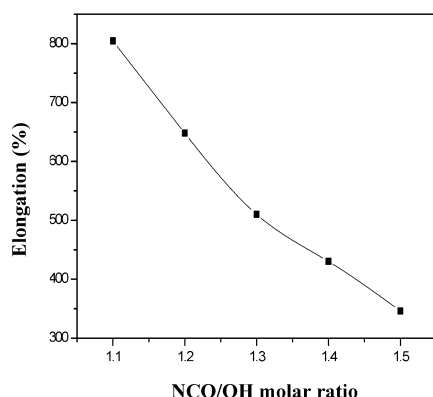


Fig. 4 Effects of NCO/OH molar ratio of PU dispersions on elongation of PU/PA LIPNs

deal of interpenetration and entanglement occurs between the two polymers, and a synergistic effect may be easy to produce; thus it may lead to an improvement of mechanical properties of PU/PA LIPNs. However, with a further increase of PA content, the miscibility of the two polymers may become worse, which can lead to phase separation between hybrid emulsions, and to a deterioration in their mechanical properties.

Effects of different components of PU dispersions on mechanical properties of PU/PA LIPNs

The effect of different NCO/OH molar ratios of PU dispersions on mechanical properties of PU/PA LIPNs is shown in Figs. 3 and 4. It is seen that with an increase in the NCO/OH molar ratio of PU dispersions, the tensile strength of PU/PA LIPNs increases, while the elongation at break of PU/PA LIPNs decreases correspondingly. This is because the content of hard segments in PU components increase with the NCO/OH molar

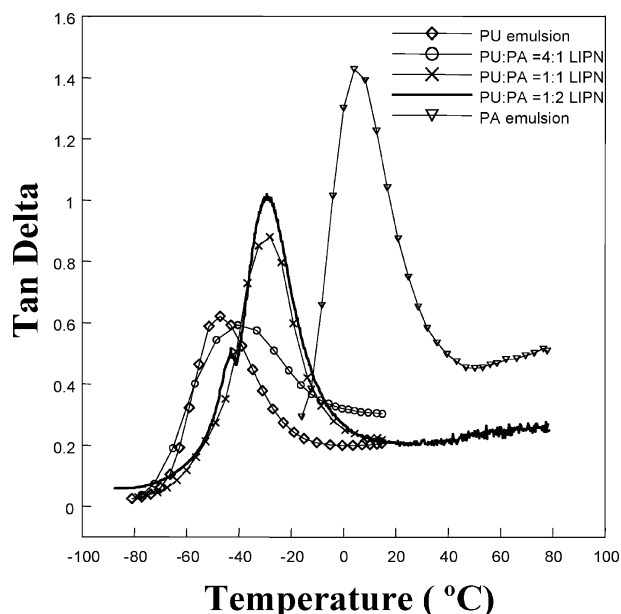


Fig. 5 Relation of $\tan \delta$ value to temperature for LIPNs with different components of PU/PA

ratio in PU dispersions, and this leads to the increase in the tensile strength of PU/PA LIPNs. In contrast, the content of soft segments in PU dispersion decreases with the increase of NCO/OH molar ratio in PU dispersions, which leads to the decrease of elongation at break of PU/PA LIPNs.

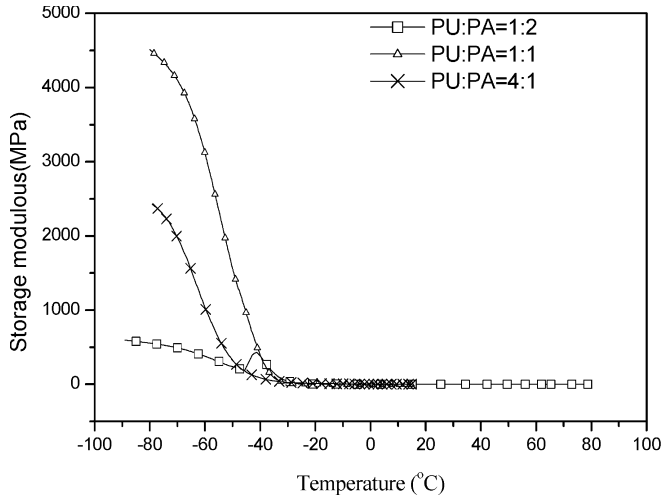
DMA characterization of PU/PA LIPNs

The dependence of the loss tangent on the temperature for different components PU/PA LIPNs is shown in Fig. 5. In the case of PU dispersions, the loss tangent exhibits a maximum at -48.24°C corresponding to the glass transition temperature (T_g). In the PU/PA LIPNs, the location of this transition is shifted to higher temperature, which indicates that compatibility between the components of the PU/PA LIPNs is increased. When the PA content in PU/PA LIPNs is lower than 50%, there is only one peak of $\tan \delta$. With a further increase in PA content, the extent of the shift of its T_g to high temperature decreases and the semi-peak width of its $\tan \delta$ becomes smaller (as shown in Table 3). When the PA content reaches 67%, there are two glass transition temperatures, which indicates that there is a weak phase separation between two polymers, also the $\tan \delta$ maximum values of the LIPNs increase with the formation of LIPNs.

The storage modulus (E') of LIPNs with varying PU/PA ratio as a function of temperature are shown in Fig. 6. The E' curve decreases with increasing temperature. When PU/PA ratio of LIPNs is 4:1, the E' curve

Table 3 Glass transition temperatures of different components PU/PA LIPN

Sample	PU:PA weight ratio	PA content (%)	T_{g1} (°C)	$\tan \delta_{\max}$	T_{g2} (°C)	Semi-peak width of $\tan \delta$ (°C)
1	1:0	0	-48.24	0.62	—	15
2	4:1	20	-39.07	0.59	—	25
3	1:1	50	-28.12	0.88	—	16.5
4	1:2	67	-30.61	1.00	-42.5	11
5	0:1	100	10.57	1.43	—	12.5

**Fig. 6** Relation of storage modulus to temperature for LIPNs with different components of PU/PA

formed a plateau within the range from -80°C to -40°C . However the plateau of the E' curve did not appear when the PU/PA ratio of LIPNs was 1:2, and 1:1 respectively. This indicated that the compatibility of PU/PA LIPNs when PU/PA ratio is 4:1 is much better than that of other two kinds of PU/PA LIPNs [12].

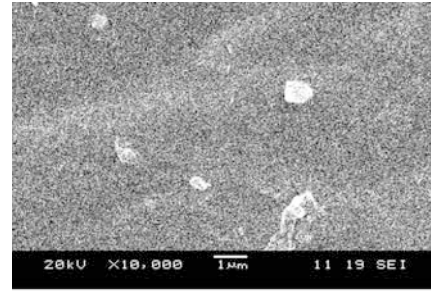
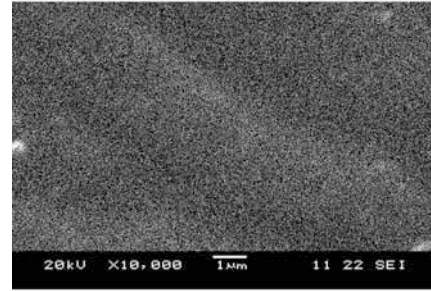
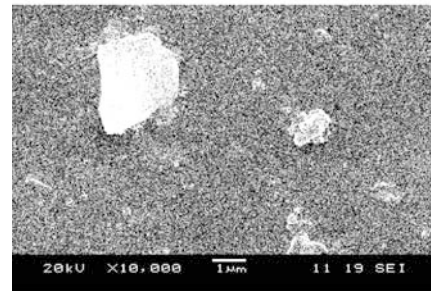
SEM of PU/PA LIPNs

The morphology of PU/PA LIPNs is observed by SEM photos (shown in Fig. 7). It shows that the phase domains of PU/PA LIPNs are increased with increased PA content of PU/PA LIPNs, and the compatibility between PU phase and PA phase is decreased, which is confirmed by their DMA measurements correspondingly.

The particle size of PU/PA LIPN emulsions

Effects of PA content on the particle size of PU/PA LIPN emulsions

PU/PA LIPN emulsions were prepared by polymerizing a mixture of acrylic monomers in the presence of a

**a)** PU: PA=1:1**(b)** PU: PA=4:1**(c)** PU:PA=1:2**Fig. 7** SEM micrographs of PU/PA LIPNs

PU dispersion, which was used as a seed. The weight ratio between PA component and PU component was varied by changing the amount of the PA introduced while keeping the amount of PU dispersion constant. The average particle size of PU/PA LIPN emulsions measured by DLS is shown in Fig. 8. With the increase of PA content, the average particle size of PU/PA LIPN emulsions is increased in a non-linear manner. When the amount of PA content is increased from 0 to 33%, the average particle size of PU/PA LIPN emulsions is almost the same as that of the PU dispersion which is used as a seed. Further increase of PA content in PU/PA LIPN emulsions results in a marked increase in the average particle size. This is because further introduction of acrylic components makes it difficult for the micelle-forming PU component to contain acrylic components and to form stable LIPN emulsion particles. Therefore larger emulsion particles are

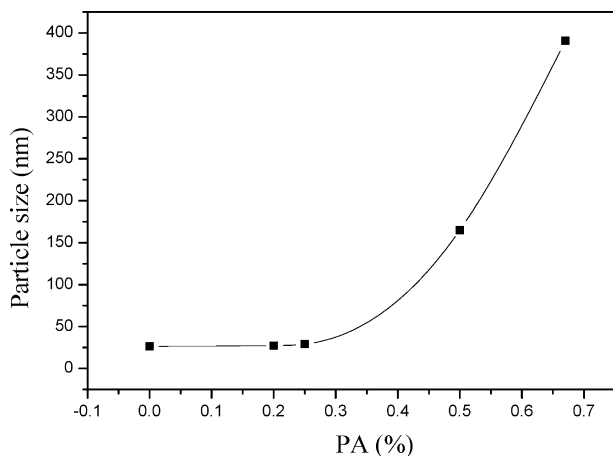


Fig. 8 Effects of PA content on the particle size of PU/PA LIPN emulsions

formed presumably by the fusion of several particles. When more acrylic components are introduced, the fusion of particles further proceeds to form much larger particles [7].

Effects of NCO/OH molar ratio of PU dispersions on the particle size of PU/PA LIPN emulsions

When the PU/PA ratio is 1:1, the effect of different NCO/OH molar ratios of PU dispersions on the particle size of PU/PA LIPN emulsions is shown in Fig. 9. With the increase of NCO/OH molar ratio of PU dispersions, the urea content in PU dispersion is increased. The presence of more hydrogen bonding can result in the aggregation between PU molecules. Consequently the average particle size of PU/PA LIPN emulsions is also increased with NCO/OH molar ratio of PU dispersions.

Conclusions

From the current work the following conclusions can be drawn:

1. PU/PA LIPNs markedly improve the water resistance of PU latex.
2. Comparing PU/PA LIPNs with their polymer physical blending counterparts, it is found that the

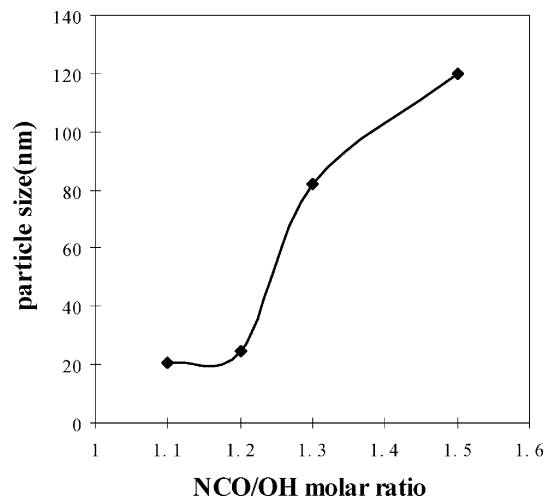


Fig. 9 Effects of NCO/OH molar ratio of PU dispersions on the particle size of PU/PA LIPN emulsions

compatibility of PU/PA LIPNs improves significantly because of a great deal of interpenetration and entanglement, and the mechanical properties such as the tensile strength and the elongation at break of PU/PA LIPNs are twice as good as those of the physical blends.

3. Analysis of the mechanical properties of PU/PA LIPNs shows that the tensile strength of PU/PA LIPNs presents a maximum value at 33 wt% PA content, while the elongation at break has a maximum value at 25 wt% PA content. Moreover, with the increase of the NCO/OH molar ratio of PU dispersions the tensile strength of PU/PA LIPNs improves and the elongation at break of PU/PA LIPNs decreases correspondingly.
4. On the basis of DMA and SEM analysis, it can be concluded that, as the PA weight content in PU/PA LIPNs increases, the phase domains become larger and the compatibility between the PU phase and the PA phase gradually decreases.
5. The particle size of PU/PA LIPNs was measured by DLS. The results show that, as the molar ratio of NCO/OH in PU dispersions increases, the particle size of PU/PA LIPNs increases, and the average particle size of PU/PA LIPNs become larger with the increase of PA content in PU/PA LIPNs.

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