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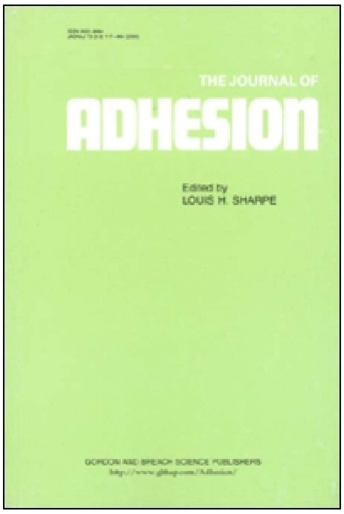

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Improved Adhesion of Waterborne Polyurethanes by Hybridizations

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Aqueous polyurethane dispersions based on isophorone diisocyanate (IPDI), poly (tetramethylene adipate) glycol (PTAd), and dimethylolproprionic acid (DMPA) were synthesized by a prepolymer mixing process. Effects of the molecular weight of PTAd and types of hybridizations, viz. blending, semi-interpenetrating polymer network (IPN), and full IPNs with polybutylacrylate have been determined. It was found that thermal, mechanical, and adhesion properties of the polyurethane dispersions increased with increasing molecular weight of polyols.

Regarding the effects of hybridization, full IPNs gave the greatest tensile strength and elongation at break with a fast drying rate, whereas semi-IPNs gave the greatest initial as well as final adhesion, implying that a certain degree of chain mobility would augment the penetrations of adhesive molecules into the soft polyurethane foam substrates.

Keywords: Adhesion; Crystallization; Interpenetrating networks (IPN); Phase separation; Polyurethanes

1. INTRODUCTION

Waterborne polyurethanes (PU) can be formulated with little or no solvent and, hence, they are nontoxic, nonflammable, and do not pollute the air. Such environmental advantages coupled with increasing solvent price have steadily expanded their usages in a number of applications in textile coatings, fiber sizings, and adhesives for many polymeric and glassy surfaces [1–3].

However, due mainly to the dispersion nature of the ionic centers of waterborne PU, certain properties including water resistance, solvent

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resistance, etc. are generally inferior to the solventbornes, and these problems need to be overcome. A number of methods to modify the waterborne PU have been suggested and some of them have been put into practice [4–6].

Latex interpenetrating polymer network (LIPN) combines two or more networks in a single latex particle. A crosslinked polymer I forms the seed latex, and upon the addition of monomer II that is swelled in seed the latex, LIPN having a core-shell structure is obtained [7]. LIPNs are usually synthesized by a sequential emulsion polymerization method, and morphologies of latex particles and cast films are controlled by the monomer feeding sequence and the interaction between polymers [8,9].

IPNs are an intimate combination of two or more crosslinked polymers that frequently consist of one elastic and one plastic network [10–12]. For example, IPN gives a reinforced rubber if the elastomer phase is continuous and predominant, or a high impact plastic if the glassy phase is continuous. In comparison with other simple blends, restricted phase separation of IPN enhances mechanical properties owing to increased physical crosslinkings which induces permanent entanglement [13].

In this article, effects of crystalline soft segment length in PU dispersions and type of hybridizations *i.e.*, semi-IPN, full-IPN, and emulsion blend of PU with polybutyl acrylate (PBA) have been studied in terms of particle size, mechanical and dynamic mechanical properties, and adhesion properties.

2. EXPERIMENTAL

2.1. Materials

Extra pure grade of isophorone diisocyanate (IPDI, Aldrich, St. Louis, Missouri), dibutyltin dilaurate (DBTDL, Aldrich) and potassium persulfate (KPS, Aldrich) were used as received. Dimethylol proprionic acid (DMPA, Aldrich) and 2,2-azobisisobutyronitrile (AIBN, Aldrich) were purified by recrystallization and dried at room temperature for 48 hrs *in vacuo*. Poly (tetramethylene adipate)glycol (PTAd, $M_n = 2000$, Aldrich) and 1,4-butane diol(1,4-BD, Aldrich) were dried for 5 hrs at 80°C under vacuum before use. Extra pure grades of triethylamine (TEA, Fluka, Milwaukee, Wisconsin), diethylene triamine (DETA, Aldrich) were dried over 3Å molecular sieve before use. Butyl acrylate monomer (Aldrich), acrylic acid (Aldrich) and crosslinking agent (divinyl benzene, Aldrich) were purified and dried by fractional distillation and stored under inert atmosphere.

TABLE 1 Formulation of PU Prepared With PTAds of Different Molecular Weights (M_n)

Sample	M_p	PTAd (M_w)	DMPA (wt. %)	1,4-BD (wt. %)	DETA (wt. %)	Soft content (wt. %)	Solid content (Soft + Hard segments) (wt. %)
PTAd-2	10000	2000	3.5	0.3	0.66	75	30
PTAd-3	10000	3000	3.5	1.1	0.66	75	30
PTAd-4	10000	4000	3.5	1.5	0.66	75	30

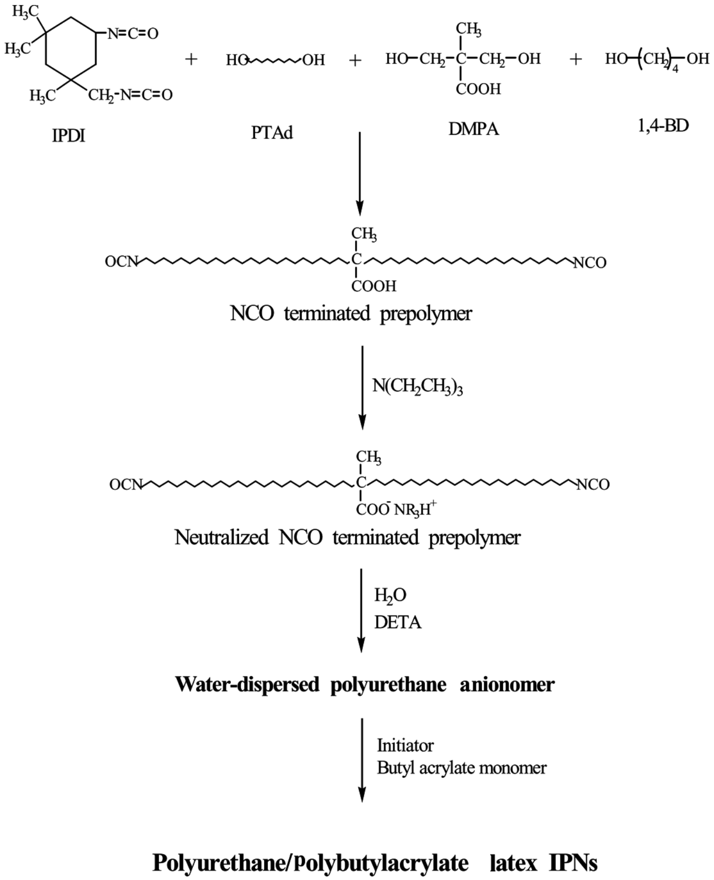
The substrate was a soft polyurethane foam, Grade KHL-1, Kyungnam Urethane Co., Kimhae, Korea.

2.2. Synthesis

The basic formulation of PU, latex IPNs, and emulsion blend are given in Tables 1 and 2. The procedures to obtain PU dispersions are shown schematically in Scheme 1 and described below. Also, Scheme 2 is shown for the conformations of PU, semi-, and full IPNs, and emulsion blend of PU with PBA. A 500 ml four-neck round bottom separable flask equipped with mechanical stirrer, thermometer, and condenser with drying tube and N_2 inlet was used as reactor. First, waterborne PUs having prepolymer molecular weight (M_p) of about 7000 were synthesized. For this IPDI, 1,4-BD, DMPA(2.8 wt.-% based on base PU), PTAd, and DBTDL (0.03 wt.-% based on base PU) were mixed and reacted at 80°C to obtain NCO-terminated prepolymer. The change of NCO value during reaction was determined using a standard dibutylamine back titration method [14]. Then, NCO-terminated prepolymer was cooled to 60°C, and TEA was added to neutralize the ionic centers. PU seed latex was obtained by adding water to the neutralized NCO-terminated prepolymer, followed by chain extension with DETA.

TABLE 2 Formulation of of PU, Semi-, and Full-IPNs, and Emulsion Blend of PU With PBA

Sample	M_p	PTAd (M_w)	Butyl acrylate (wt. %)	Divinyl benzene (phr)	Acrylic acid (wt. %)	Initiator
PU	7000	2000	0	0	0	—
Semi-IPN	7000	2000	20	0	0	KPS
Full-IPN	7000	2000	20	4	0	KPS
Emulsion blend	7000	2000	20	0	7	AIBN

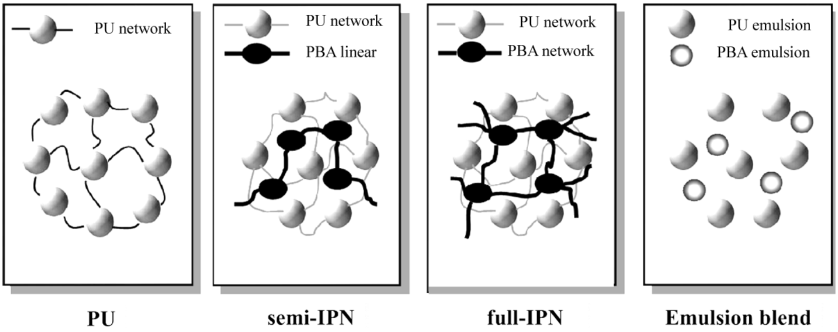


SCHEME 1 The synthesis process of PU/PBA latex interpenetrating polymer network.

LIPNs were prepared by a sequential and two-stage polymerization method. Mixture of monomer, crosslinking agent (when applied), and KPS (0.5 wt.-% of base monomers) were added to the seed latex and heated to 60°C for three hours to obtain PU LIPN with PBA. The resulting product was a stable emulsion with solid content of about 30%.

2.3. Characterizations

Particle size of the systems was measured by a light scattering method (Brookhaven BI-2000SM, Brookhaven Instruments Corporation, Holtsville, New York) at room temperature [15]. Films were prepared



SCHEME 2 Conformation of PU, semi-, and full-IPNs, and emulsion blend of PU with PBA.

by casting the emulsion on a Teflon® plate, followed by drying at 60°C for 24 hrs and 80°C for 48 hrs. To measure the rate of drying, the weight of water (W_o) in the LIPN emulsion was measured as a function of drying time during the film casting, according to

$$Water\ content\ (\%) = \frac{W_o - W}{W_o} \times 100,$$

where W is the weight of evaporated water in the LIPN emulsion.

Tensile properties of cast films were measured using a tensile tester (Tinius Olsen, Easton, Pennsylvania) at a crosshead speed of 500 mm/min, and an average of at least five measurements were taken to report. Dynamic mechanical properties of the cast films were measured with a DMTA (Rheometrics MK3E, Piscataway, New Jersey) from -100 to 200°C at 10 Hz and a strain of 0.05 with a sample size of $0.5 \times 5 \times 8$mm.

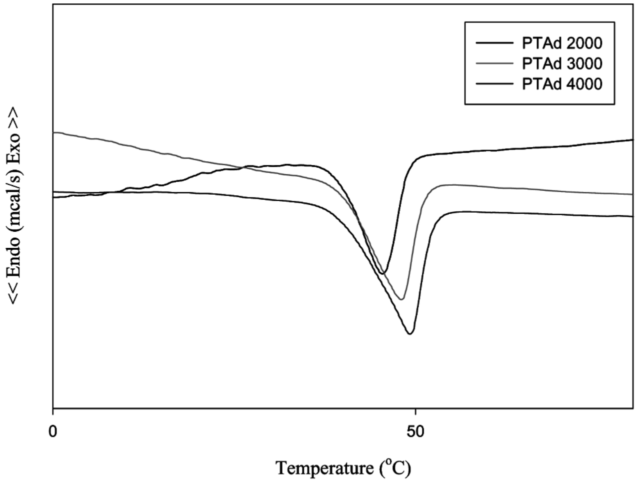
The crystalline structures were examined with an X-ray diffraction spectrometer (XRD) (Rigaku, Tokyo, Japan) using CuKα radiation (40 kV, 50 mA). Dispersion cast films were mounted for measurement in the through direction. Thermal properties (melting temperature [T_m] and the melting enthalpy of PU) were measured using a DSC3100S (MAC Science, Tokyo, Japan). Aluminium cells containing 5 mg of PU films were heated from -100 to 100°C and the heating rate was 10°C/min.

For T-peel tests two adherends (of the soft PU foam) of equal thickness were bonded with an adhesive, *viz*. PU dispersion. Stress was applied at a line at a commonly used angle of peel in tests, 180° for the adherends (ASTM D1876). Two types of strength *i.e.*, initial adhesive strength (test after 30 min of bonding) and final adhesive strength (test after 1 day) were measured.

3. RESULTS AND DISCUSSION

3.1. Effects of Soft Segment Length

Figure 1 shows the DSC thermograms of PU prepared with PTAds of different molecular weights (M_n). It is seen that peak (melting) temperature (Tm) monotonically increases from 45.4 to 49.2°C as the M_n of PTAd increases from 2000 to 4000. It is generally known that shorter soft segments are more compatible with hard segments since they have more urethane groups, which are compatible with hard segments. Therefore, soft segments prepared from PTAd of higher M_n are more likely to be phase separated to a greater extent than for hard segments. With a greater phase separation, PTAd segments of higher M_n can be crystallized to a greater extent to give greater heat of fusion. The increase of melting temperature is attributed to an increase in the size of the crystallites [16].



	Peak Position(°C)	Peak Area($cal \cdot g^{-1}$)
PTAd-2	45.4	5.63
PTAd-3	47.9	6.61
PTAd-4	49.2	7.75

FIGURE 1 The DSC thermograms of PU prepared with PTAds of different molecular weights (M_n).

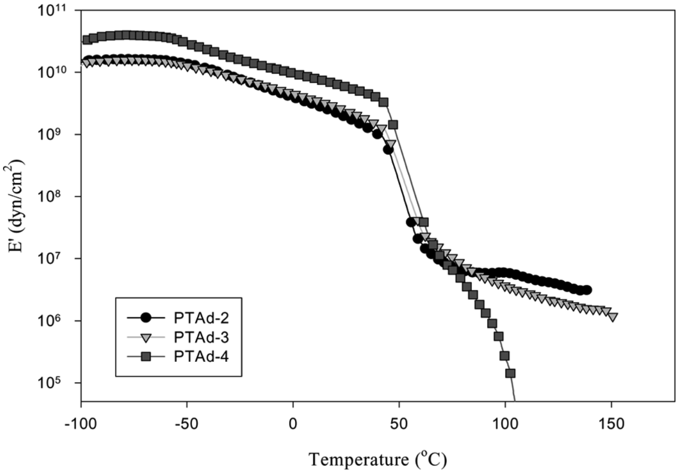


FIGURE 2 Storage moduli of PU prepared with PTAds of different molecular weights (M_n).

Figure 2 shows the dynamic mechanical properties of the dispersion-cast films. A large drop of storage modulus at about 50°C corresponds to the melting transition of the soft segments, whereas a point of inflection at about -50°C is the glass transition temperature (Tg) of the soft segments. It is seen that the soft segment based on PTAd 4000 gives a lower Tg than the others, which is an indication of great soft segment-hard segment phase separation. As the phase separation increases, the Tg of soft segments generally decreases and that of hard segments increases.

PUs from PTAd 2000 and PTAd 3000 show fairly well-defined rubbery plateaus which are extended up to about 150°C. However, PU from PTAd 4000 shows a drop at about 100°C and does not show a rubbery plateau. Above the melting temperature of soft segments, hard segments alone carry the load and the weight fraction of hard segments, which increases with decreasing M_n of PTAd, seems to govern the high temperature properties.

Initial modulus, tensile strength, and elongation at break increase with increasing M_n of PTAd (Figure 3). This is mainly due to the increased crystallinity of soft segments with increasing M_n of PTAd (Figure 1).

Probably the most significant synergistic effect of high soft segment crystallinity may be found with the rate of drying and adhesion properties. Figure 4 shows that rate of drying increases with increasing M_n of

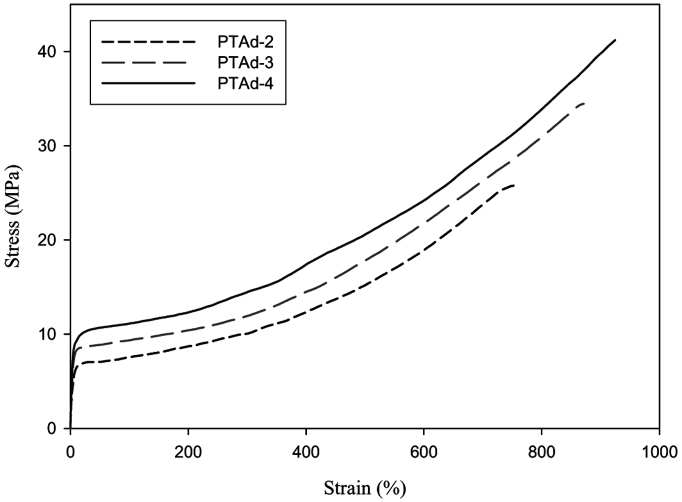


FIGURE 3 Initial modulus, tensile strength, and elongation at break of PU prepared with PTAds of different molecular weights (M_n).

PTAd probably due to the increased heat of crystallization, as well as the increased hydrophobicity of long polyol chains. Heats evolved during crystallization should speed up the drying of films. Final as well

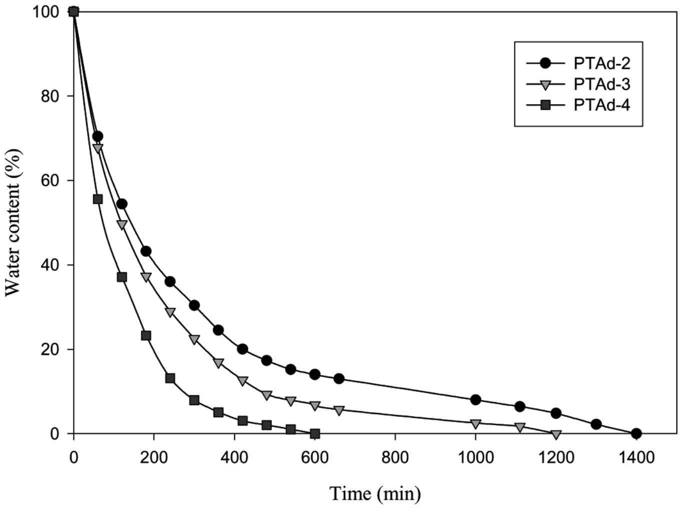


FIGURE 4 Drying rate of PU prepared with PTAds of different molecular weights (M_n).

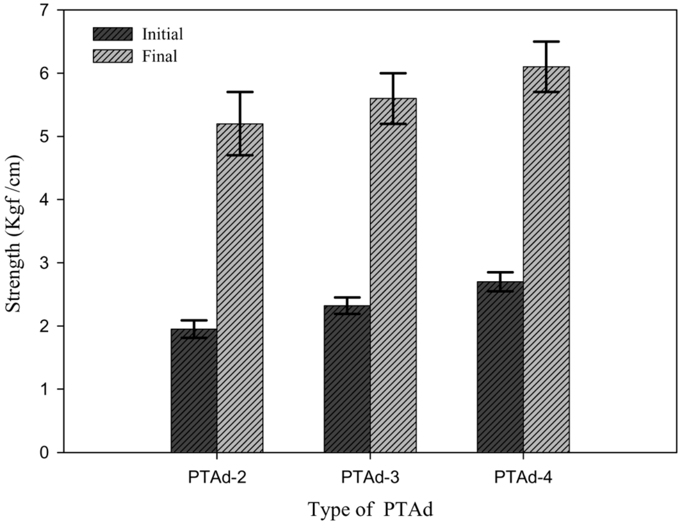


FIGURE 5 T-peel strength values of PU prepared with PTAds of different molecular weights (M_n).

as initial adhesive strength, determined from the T-peel test, monotonically increases with increasing M_n of PTAd (Figure 5). This in part is due to the lower T_g of high M_n PTAd, however, high crystallinity seems to be the key parameter that augments the adhesion. With increased crystallinity, high heat of crystallization speeds up drying in the initial stage of drying. Upon completing the drying, strong mechanical seals of the PU crystallites with the substrates at the uneven surfaces should give large final adhesive strength.

3.2. Effects of Hybridization

The average particle sizes of PU, semi-IPN, and full IPN of PU with PBA are shown in Figure 6, where the particle size increases along PU < full IPN < semi-IPN. The increase is primarily due to the inclusion of PBA in the PU particles to form an inverted core-shell morphology. The core (PBA)-shell (PU) morphology is obtained due to the greater hydrophobicity of PBA over PU. A somewhat smaller particle size of full IPN as compared with semi-IPN is probably due to the decreased uptake of water into the relatively highly crosslinked particles of full IPNs.

The XRD profiles of PU, semi-, and full IPNs, and blend cast films are shown in Figure 7. The XRD profile of the PU dispersion-cast film

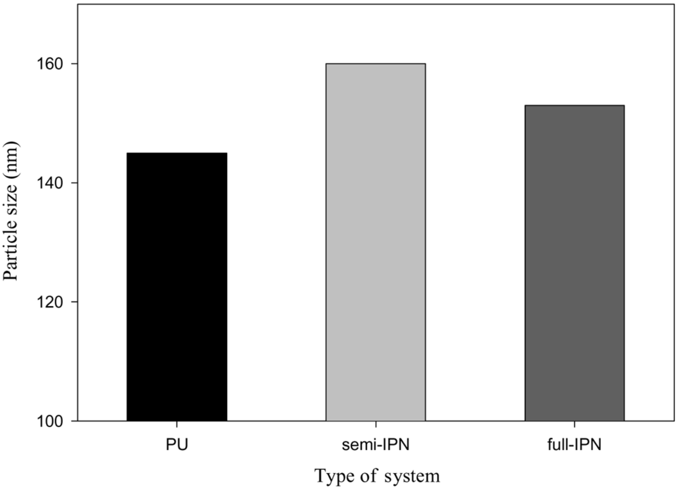


FIGURE 6 The average particle sizes of PU, semi-IPN, and full-IPN of PU with PBA.

shows the sharpest peak at about $2\theta = 21^\circ$. However, the peak intensity decreases in semi- and full IPNs, and the decrease is most pronounced with the blend. The XRD peaks of PU correspond to the

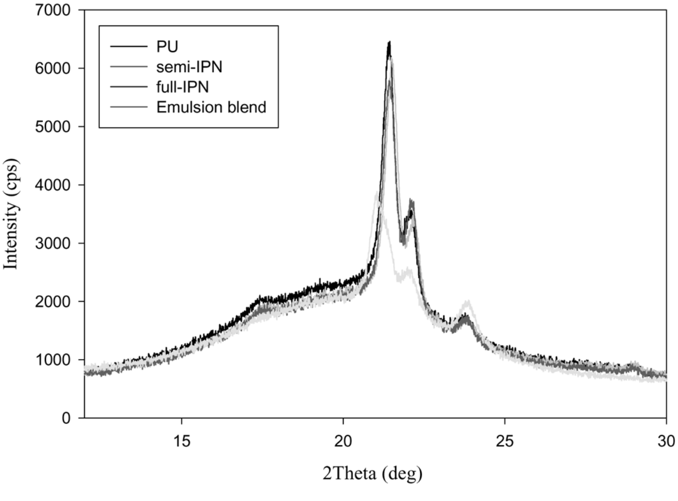


FIGURE 7 The X-ray diffraction profiles of PU, semi-, and full-IPNs, and emulsion blend cast films.

crystalline domain of the soft segment, *viz*, the PTAd. It seems that the PBA chains provide the PUs with disruptive effects, resulting in unit cell distortions. The most pronounced effect obtained with the blend is most likely due to the polar interactions of ester groups of PTAd segments with the ester groups of acrylic acid units incorporated in to PBA to make it water-dispersible.

Tensile properties of PU, semi-, and full IPNs, and emulsion blends of PU with PBA are shown in Figure 8. It is seen that both tensile

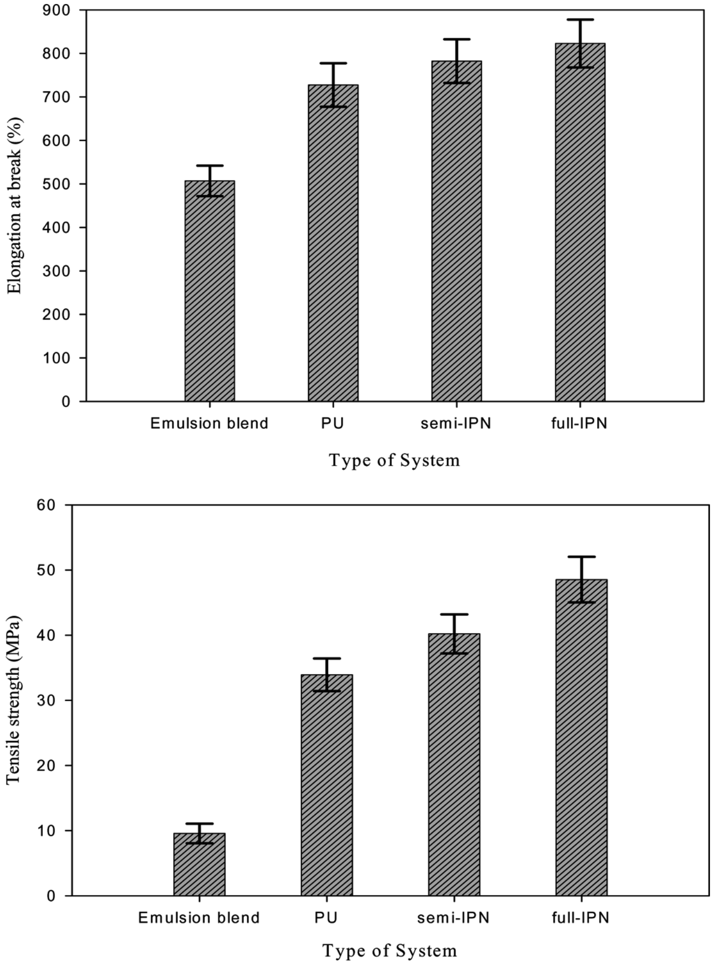


FIGURE 8 Tensile properties of PU, semi-, and full-IPNs, and emulsion blend of PU with PBA.

strength and elongation at break increase along blend < PU < semi-IPN < full IPN. In PU/PBA IPNs, BA monomers are swelled and polymerized within the PU particles in the form of either crosslinked (full IPN) or linear (semi-IPN). Ideally, PU and PBA chains are physically interlocked and permanent entanglements are introduced to suppress the PU/PBA phase separations. This often leads to a positive deviation in density and mechanical properties as well [17]. On the other hand, the decreased mechanical properties of the blend are probably due to the significantly decreased crystallinity of PU due to the specific interactions between the two ester groups of PU and PBA.

Figure 9 shows that the water content of dispersion-cast film at a given time of drying decreases along PU > blends > semi-IPN > full IPN. This indicates that the films are hydrophobically modified with the incorporation of PBA [6]. It is seen that the hybridization by full IPN gives the most effective hydrophobic modification of the PUs.

The results of T-peel tests are shown in Figure 10, where the highest adhesive strength is obtained with semi-IPN and the lowest with emulsion blend for both initial and final adhesion. Initial adhesion should depend on a number of factors such as glass transition temperature of the adhesive, crystallization kinetics, interpenetrating degree in IPNs, etc. It seems that the semi-IPN is favorably matched in this regard. The poorest adhesive strength of the blends should

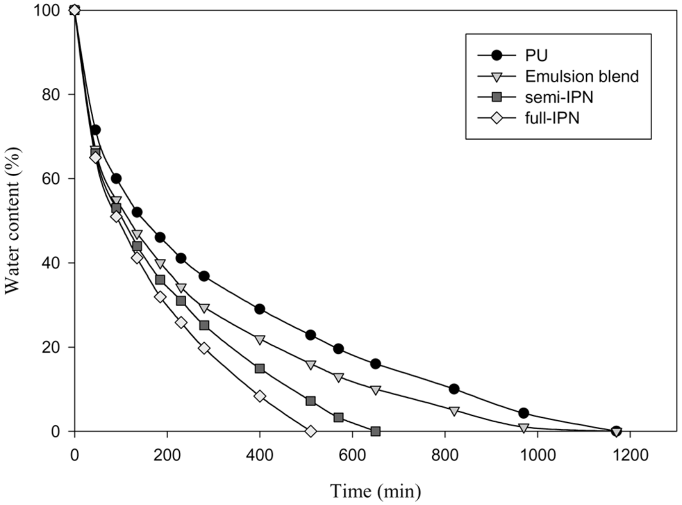


FIGURE 9 Drying rate of PU, semi-, and full-IPNs, and emulsion blend of PU with PBA.

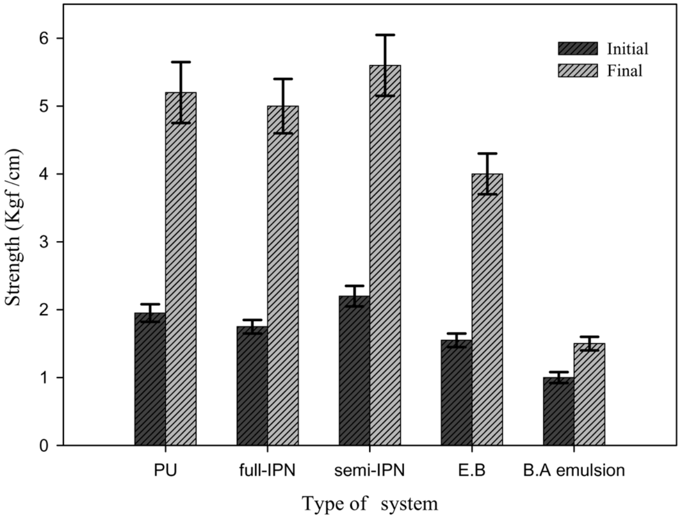


FIGURE 10 T-peel strength values of PU, semi-, and full-IPNs, and emulsion blend of PU with PBA.

come from the lowest crystallinity which gives slow drying and poor mechanical seals upon complete drying.

4. CONCLUSIONS

With increasing molecular weight of PTAd, thermal, mechanical, and adhesion properties of PUs were improved due to the well-organized structures of soft segments with a great degree of phase separation between soft and hard segments.

Regarding the effects of hybridization, full IPN gave the greatest tensile strength and elongation at break with fast drying rate, whereas semi-IPN gave the greatest initial as well as final adhesion, implying that a certain degree of chain mobility would augment the penetrations of adhesive molecules into the substrates.

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