Modification of Aqueous Polyurethane Dispersions via Tetraphenylethane Iniferters

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ABSTRACT: Aqueous polyurethane (PU) dispersions containing tetraphenylethane iniferter groups were prepared from 4,4′-diphenylmethane diisocyanate, poly(propylene oxide)glycols, dimethylol propionic acid, and 1,1,2,2-tetraphenylethane-1,2-diol. To improve the water resistance of the dispersions, methyl methacrylate monomers were added into these dispersions and block-copolymerized onto the main PU chain. The viscosity and particle size of the dispersions were determined. Dispersion-cast films were characterized in terms of the contact angle, the swell in water, and the mechanical properties. Contact-angle and water-swell measurements showed that the hydrophilicity of the films was decreased significantly when methyl methacrylate was polymerized in the presence of tetraphenylethane containing aqueous PU dispersions. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2993–3000, 1999

Key words: polyurethane dispersion; macroiniferter; ionomer; PMMA

INTRODUCTION

The physical and chemical properties of polyurethane (PU) depend on the type and composition of polyol, diisocyanate, the chain extender, and other additives. Conventional PU is hydrophobic in nature, but when ionic groups are incorporated, PU with both hydrophobic and hydrophilic segments is obtained, which, in turn, forms a dispersion when water is added. Cationic,[1,2] anionic,[3–7] and zwitterionomeric[8] PUs have been successfully used to prepare dispersions. But incorporation of ionic groups into the PU backbone reduces the water resistance of the films derived from the dispersions. To overcome this drawback, postpolymer modification of the dispersions has been carried out through grafting of hydrophobic monomers onto the PU backbone.[9,10] In our laboratory, for the same purpose, PU dispersions consisting of terminal double bonds have been reacted with hydrophobic acrylate monomers and improved water resistance of the films has been obtained.[11]

PU macroiniferters (iniferter[12] is an initiator, transfer agent, and/or terminator in radical polymerization), which consist of tetraphenylethane groups in the PU backbone, have already been synthesized and used to obtain homopolymers and block copolymers[13–19] through "living" radical polymerization. With iniferters, controlled radical polymerization of vinyl monomers is possible and well-defined polymers can also be obtained through this method. In this article, the synthesis, characterization, and modification of tetraphenylethane groups incorporated into PU ionomeric dispersions are discussed.

EXPERIMENTAL

Materials

Poly(propylene oxide)glycols (PPGs) of molecular weights 1000 (PPG1000), 2000 (PPG2000), and

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Table I Preparation of PU Dispersions Containing Tetraphenylethane Groups

	Prepolymer Stage (60°C)								Chain Extension Stage[a] (30°C)				Dispersion Stage[b] (30°C)			
	PPG			MDI		DMPA			TPED		DMF	DBTD[c]	TEA		Water	% of
Code	Mol Wt	Moles	Wt (g)	Moles	Wt (g)	Moles	Wt (g)	%	Moles	Wt (g)	Vol (mL)	(g)	Moles	Wt (g)	(mL)	Neutraln
6P2N	2000	0.0050	10.0	0.02	5.0	0.0090	1.2072	6.2	0.006	2.1988	39.1	0.2525	0.0090	0.9107	71.8	100
6P290	2000	0.0050	10.0	0.02	5.0	0.0090	1.2072	6.2	0.006	2.1988	39.0	0.2525	0.0081	0.8196	71.4	90
6P280	2000	0.0050	10.0	0.02	5.0	0.0090	1.2072	6.2	0.006	2.1988	38.8	0.2525	0.0072	0.7286	71.1	80
6P1N	1000	0.0068	6.8	0.02	5.0	0.0072	0.9657	6.1	0.006	2.1988	31.9	0.2525	0.0072	0.7286	58.4	100
6P4N	4000	0.0033	13.2	0.02	5.0	0.0107	1.4352	6.2	0.006	2.1988	46.3	0.2525	0.0107	1.0827	85.3	100
5P2N	2000	0.0060	12.0	0.02	5.0	0.0080	1.0730	5.0	0.006	2.1988	42.7	0.2525	0.0080	0.8095	78.2	100
7P2N	2000	0.0040	8.0	0.02	5.0	0.0100	1.3413	7.5	0.006	2.1988	35.6	0.2525	0.0100	1.0119	65.3	100

[a] Solid content = 33.3%.
[b] Solid content = 15%.
[c] 2 mol % based on MDI.

4000 (PPG4000) were dried under reduced pressure at 105°C for 3 h before use. 4,4′-Diphenylmethane diisocyanate (MDI) was purified using a hot filter funnel. Dimethylol propionic acid (DMPA; Aldrich, Milwaukee, WI) was dried in a hot air-circulating oven at 105°C before use. 1,1,2,2-Tetraphenylethane-1,2-diol (TPED) was synthesized[20] from benzophenone and 2-propanol using acetic acid as a photosensitizer. *N,N′*-Dimethylformamide (DMF) was distilled at reduced pressure and the middle portions were stored over molecular sieves (type 4 Å) until use. Methyl methacrylate (MMA) was washed with 5% aqueous NaOH and distilled at reduced pressure, and the middle portions were stored at 0–4°C until use. Dibutyltin dilaurate (DBTDL) was used as received and triethylamine was used after storing over type 4 Å molecular sieves.

Methods

The particle size was measured using a Malvern IIC autosizer. Viscosities of the dispersions were measured at 20°C using a Brookfield viscometer. Contact angles were measured at room temperature by dropping water onto the films using an Erma G-1-type instrument. Tensile properties of the films were determined using a Tinius Olsen 1000 tensile tester at a crosshead speed of 100 mm/min. Tensile specimens were prepared according to the ASTM D-412 method. The swell in water was measured at room temperature by immersing a film into water until the film was in equilibrium with water. The percentage of swelling was calculated by

$$\%\ \text{swell} = \frac{W - W_0}{W_0} \times 100$$

where W_0 and W are the original and equilibrium weights of the film, respectively.

Synthesis of PU Dispersions

Calculated amounts of MDI, DMPA, and previously dried PPG were taken in a four-necked round-bottom flask fitted with a N_2 gas inlet, mechanical stirrer, separating funnel, and condenser attached to a $CaCl_2$ guard tube. Then, the reaction mixture was stirred at 60°C under a N_2 atmosphere. When the isocyanate value reached the required value as determined by dibutylamine back titration,[21] the temperature was reduced to 30°C and calculated amounts (cf. Table

Table II Modification of PU Dispersions Through Copolymerization with MMA at 75°C

	Dispersion			MMA			
Code		Wt (g)	Wt %	Wt (g)	Wt %	Water (mL)	Time (h)
M6P95	6P2N	57	95	3	5	—	12
M6P90	6P2N	54	90	6	10	10.5	12
M6P80	6P2N	48	80	12	20	36.0	12
M6P70	6P2N	42	70	18	30	61.5	12
M6P60	6P2N	36	60	24	40	87.0	12
M6P50	6P2N	30	50	30	50	112.5	12
M6P6	6P2N	48	80	12	20	36.0	6
M6P12	6P2N	48	80	12	20	36.0	12
M6P24	6P2N	48	80	12	20	36.0	24
M6P48	6P2N	48	80	12	20	36.0	48
M5P	5P2N	48	80	12	20	36.0	12
M7P	7P2N	48	80	12	20	36.0	12
M90	6P290	48	80	12	20	36.0	12
M80	6P280	48	80	12	20	36.0	12
M1	6P1N	48	80	12	20	36.0	12
M4	6P4N	48	80	12	20	36.0	12

I) of TPED and DMF were added. To this, 2 mol % of DBTDL based on the initial isocyanate content was added and stirring was continued for another 24 h. A calculated amount of TEA was then added and stirred for another 1 h at the same temperature. Then, the required amount of water (30°C) was added to the reaction mixture using a tubing pump at a constant flow rate as described previously.[11]

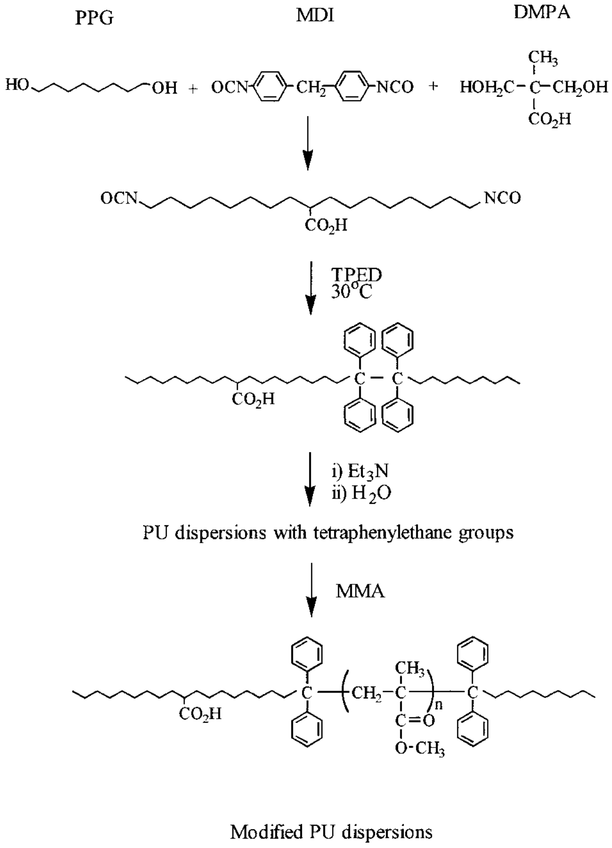
Modification of PU Dispersions

Modification of the dispersions was carried out through polymerization of MMA using tetraphenylethane groups present in the PU backbone of the dispersions. Required amounts of the dispersion were taken in a three-necked round-bottom flask fitted with a N_2 gas inlet, mechanical stirrer, and separating funnel. The dispersion was flushed with nitrogen for 15 min and then the required amounts of monomer and water were added. The reaction mixture was stirred at 300 rpm at 75°C. After the desired reaction time (cf. Table II), part of the modified dispersion was poured into Teflon sheets and kept in an air-circulating oven thermostated at 120°C for 3 h in order to form films.

RESULTS AND DISCUSSION

Dispersion Characteristics

Table I gives the synthetic details of the preparation of the PU dispersions. Since MMA is hydrophobic, it was used to hydrophobically modify the dispersions. The synthetic route is outlined in Scheme 1.



Scheme 1

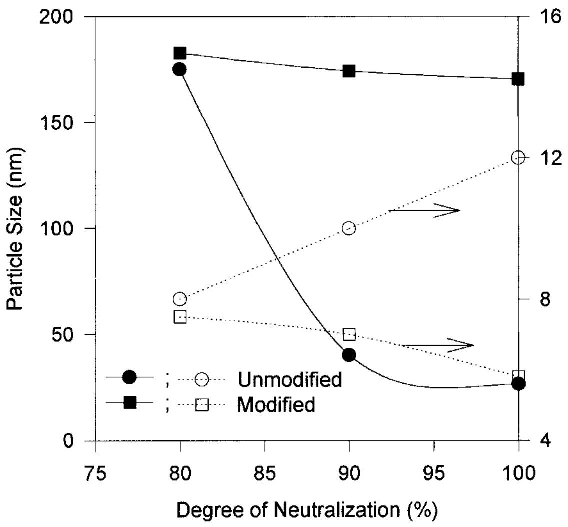


Figure 1 Particle size and viscosity of unmodified and modified PU dispersions with different degrees of neutralization.

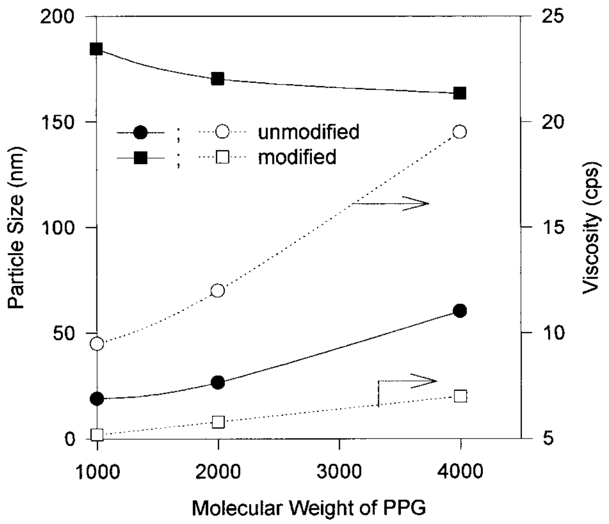


Figure 2 Effect of PPG molecular weight on particle size and viscosity of unmodified and modified PU dispersions.

Table II gives details of the modification of the PU dispersions. Figure 1 shows the particle size and viscosity of the modified and unmodified PU dispersions as a function of the degree of neutralization (6P2N, 6P290, 6P280, M7P, M90, M80). Generally, the particle size decreases with increasing degree of neutralization due to the increased hydrophilicity of the particle. Accordingly, the swell of water into the particle increases and, hence, the hydrodynamic volume of the particle and viscosity increase with increasing hydrophilicity. The dispersion viscosity is given as[22,23]

$$\frac{\eta}{\eta_s} = 1 + k_1\Phi + k_2\Phi^2 + \cdots$$

where η_s is the viscosity of the medium and the k's are constants. The decrease of the particle size with the degree of neutralization is pronounced with the unmodified dispersion, and it is small with the modified dispersion, implying that the hydrophobic modification and chain rigidity of the PMMA block govern the particle size and the viscosity as well.

Figure 2 shows the effect of the PPG molecular weight (M_n) on the viscosity and particle size of the dispersion (6P1N, 6P2N, 6P4N, M1, M2, M6P80). As the M_n of PPG increases, both the viscosity and particle size increase for the unmodified dispersions. As the M_n of PPG increases, the aliphatic chain segment and, hence, the molecular weight of the PU chains increase. The increased hydrophobicity thermodynamically augments the particle size, and the large molecular weight of PU makes breakup difficult during the dispersion with water. With the incorporation of PMMA, hydrophilicity decreases and the effect of the PPG molecular weight on the particle size and viscosity becomes less important.

Figure 3 shows the effect of the DMPA content on the viscosity and particle size of the dispersions (5P2N, 6P2N, 7P2N, M5P, M6P12, M7P). As the DMPA content increases, the ionic content

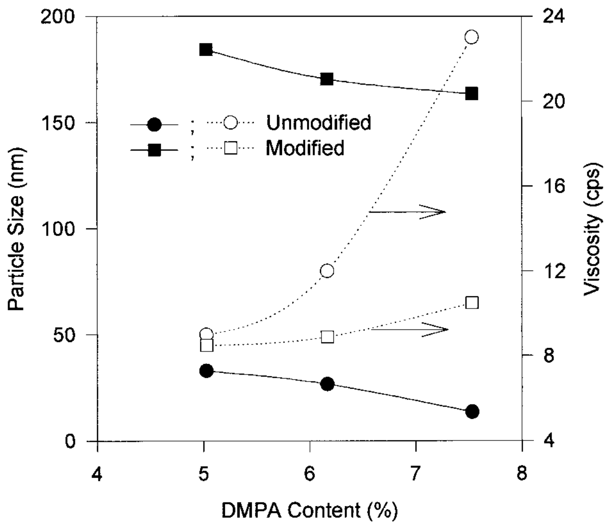


Figure 3 Particle size and viscosity of unmodified and modified PU dispersions with different DMPA content.

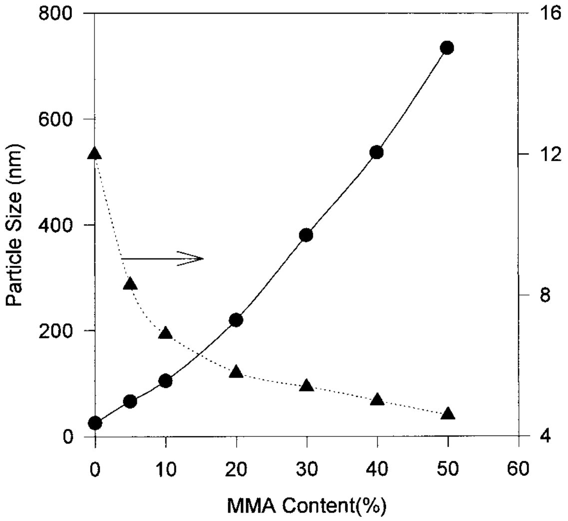


Figure 4 Effect of MMA content in the feed on the particle size and viscosity of PU dispersions.

increases. So, as the DMPA content is increased, the particle size decreases due to the increased hydrophilicity and viscosity increases due to the increased hydrodynamic volume of the particles via the swell. When MMA is incorporated, the particle size increases several times due to the increased hydrophobicity and solid content, and the viscosity of the dispersion decreases due to the decreased hydrophilicity of the particles.

Figures 4 and 5, respectively, show the effects of the MMA content and polymerization time on the viscosity and particle size of the dispersion.

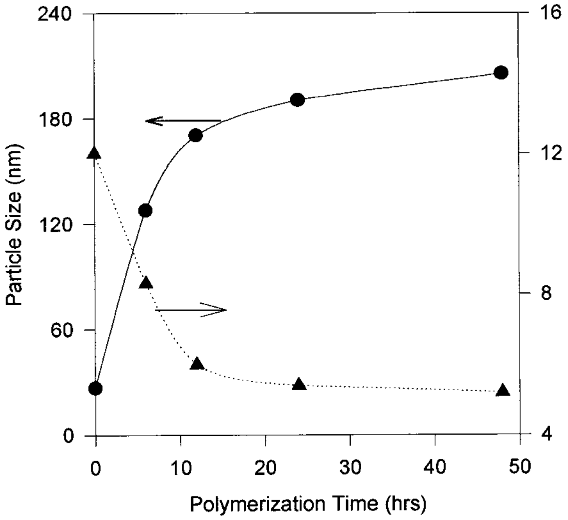


Figure 5 Effect of polymerization time on particle size and viscosity of PU dispersions.

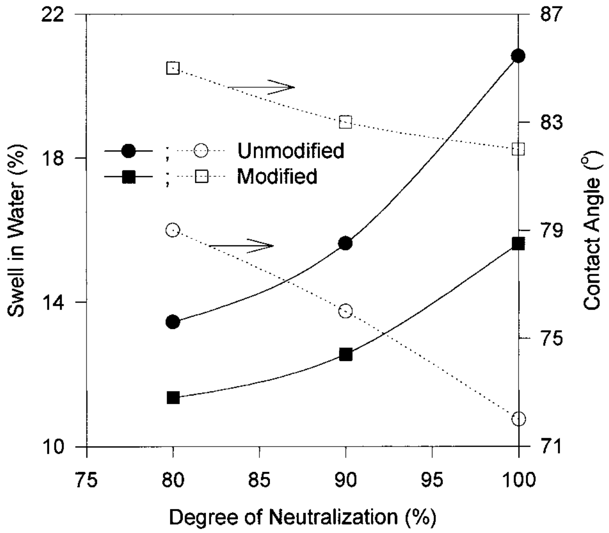


Figure 6 Effect of neutralization on contact angle and swell in water of unmodified and modified PU dispersions.

As the MMA content and polymerization time increased, the particle size increases whereas the viscosity decreases asymptotically. As the MMA content and polymerization time increase, the hydrophobicity increases and, thereby, the particle size increases and viscosity decreases. The dispersions were not stable when the MMA content in the feed was above 50%.

Contact Angle and Swell

Figures 6 and 7, respectively, show the effects of neutralization and DMPA content on the water swell and the contact angle of the dispersion-cast films. As the degree of neutralization and DMPA content increase, hydrophilicity increases and, hence, the swell in water increases and the contact angle with the water decreases. When these dispersions are modified through MMA incorporation, the water swell decreased whereas the contact angle increased. This shows that the hydrophilicity of the films decreases significantly when MMA units are incorporated.

Figure 8 shows the effect of the PPG molecular weight on the swell in water and the contact angle. As the molecular weight of PPG increases, the water swell increases and the contact angle decreases. Apparently, this is a contradiction to the increased particle size with the M_n of PPG. PUs prepared from a high M_n of PPG have more urethane linkages than do those from a low M_n of PPG since more moles of DMPA are incorporated

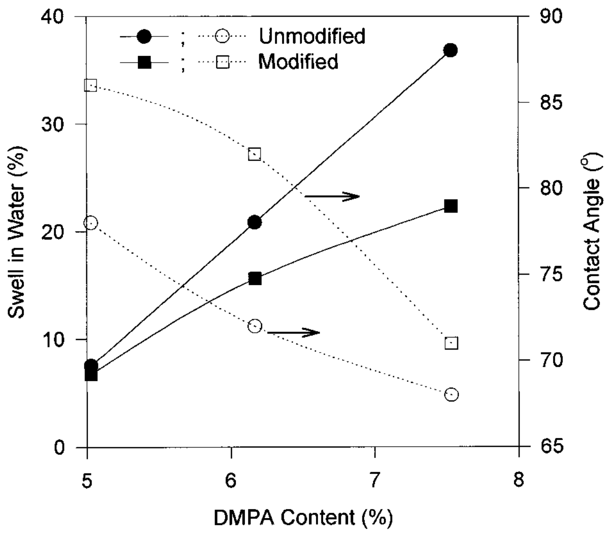


Figure 7 Effect of DMPA content on contact angle and swell in water of unmodified and modified PU dispersions.

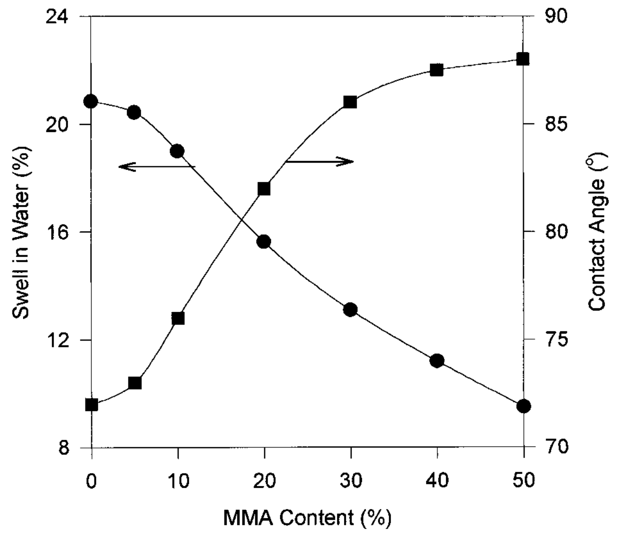


Figure 9 Effect of MMA content on contact angle and swell in water of the PU dispersions.

(0.9657 mol for PPG1000 and 1.4325 mol for PPG3000, Table I). Therefore, the total hydrophilicity of the polymer could be increased, leading to an increased swell in water and decreased contact angle when the M_n of PPG is increased.

As expected, the swell decreases and the contact angle increases when MMA is incorporated into the main chain of PU due to the decreased hydrophilicity of the films. The swell in water decreases and the contact angle increases when the MMA content in the feed (Fig. 9) and polymerization time (Fig. 10) are increased due to the increased hydrophobicity.

Mechanical Properties

As the degree of neutralization (Fig. 11) and DMPA content (Fig. 12) are increased, the tensile strength increases and the elongation at break decreases, due, respectively, to the increased ionic interactions and the increased hard fraction of

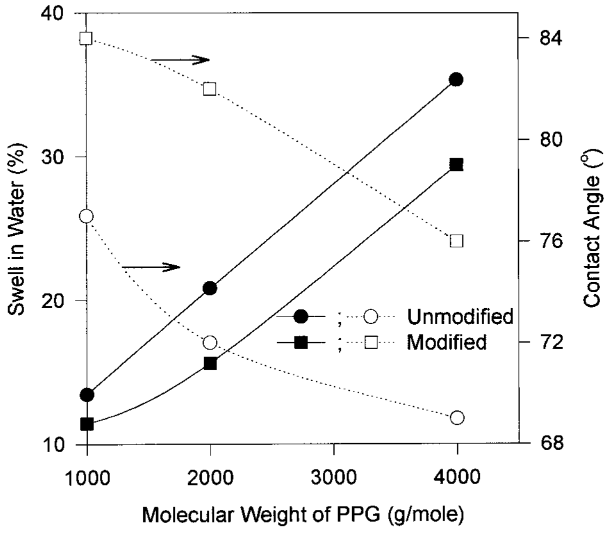


Figure 8 Effect of PPG molecular weight on contact angle and swell in water of unmodified and modified PU dispersions.

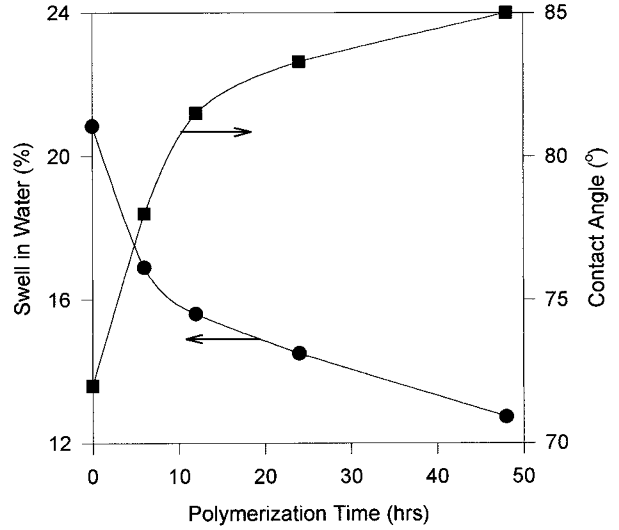


Figure 10 Effect of polymerization time on contact angle and swell in water of unmodified and modified PU dispersions.

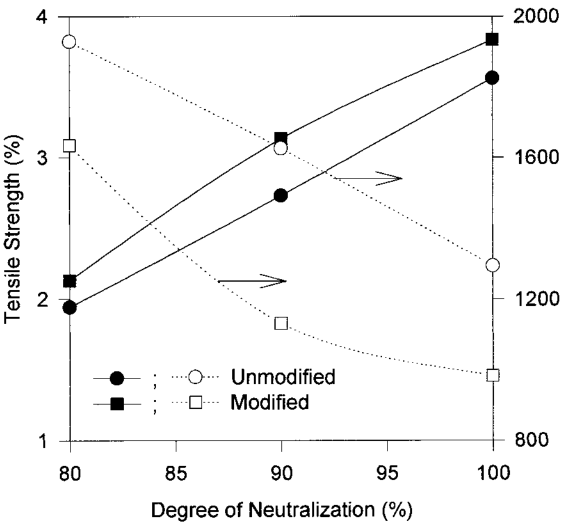


Figure 11 Tensile strength and elongation at break of the films obtained from unmodified and modified PU dispersions with different degrees of neutralization.

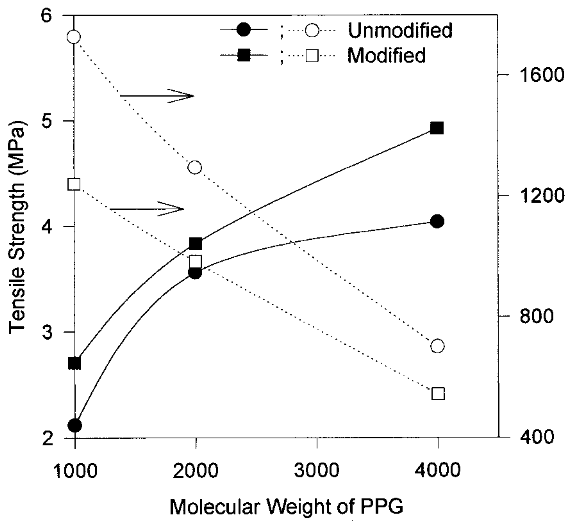


Figure 13 Effect of PPG molecular weight on tensile strength and elongation at break of unmodified and modified PU dispersion-cast films.

the films. It is seen that the effect is more pronounced with DMPA. Figure 13 shows the effect of the PPG molecular weight on the tensile strength and elongation at break of the dispersion-cast films. As the M_n of PPG increases, the tensile strength increases, whereas the elongation at break decreases. In all cases, the PMMA-incorporated films show higher tensile strength and lower elongation at break as compared with their unmodified ones. As the MMA content in the feed (Fig. 14) and polymerization time (Fig. 15) increase, the tensile strength increases and the elongation at break decreases due to more incorporation of hard PMMA blocks.

CONCLUSIONS

Iniferters groups, namely, tetraphenylethanes, were successfully incorporated into PU dispersions and these groups were used to polymerize

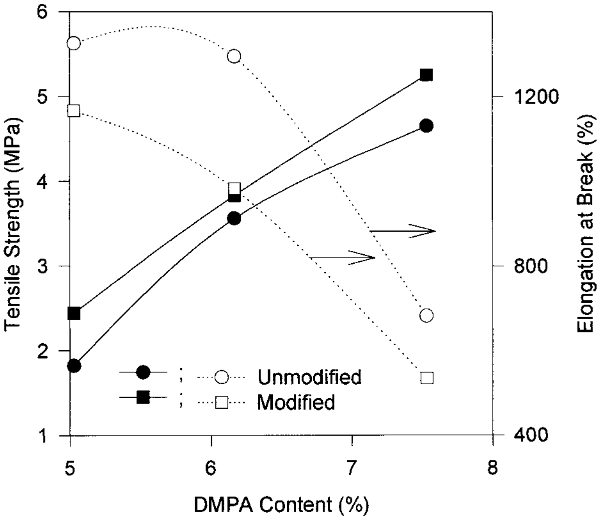


Figure 12 Effect of DMPA content on tensile strength and elongation at break of unmodified and modified PU dispersion-cast films.

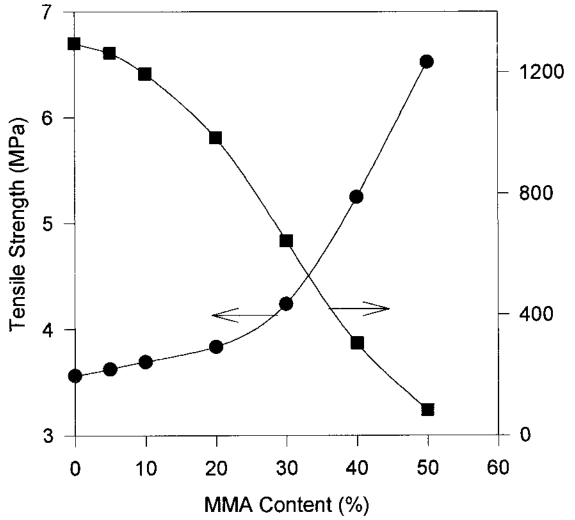


Figure 14 Effect of MMA content on tensile strength and elongation at break of the dispersion-cast films.

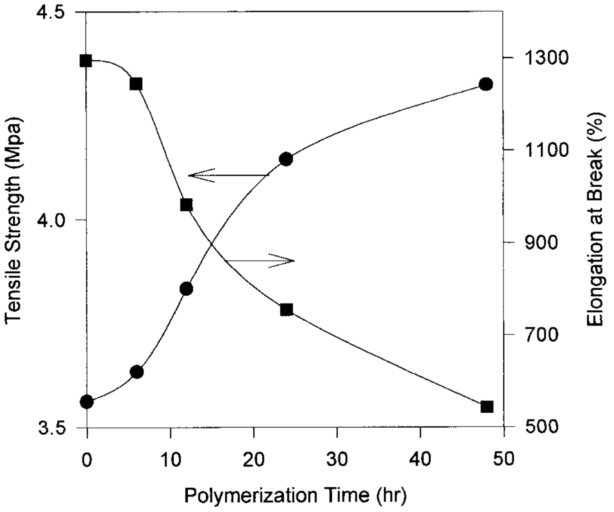


Figure 15 Effect of PMMA polymerization time on tensile strength and elongation at break of the dispersion-cast films.

MMA in order to increase the water resistance of the films derived from aqueous dispersions of PU. The effect of the degree of neutralization, DMPA content, PPG molecular weight, MMA content in the feed, and polymerization time of MMA on the viscosity and particle size of the dispersions and contact angle, swell, and mechanical properties of the dispersion-cast films was studied. The contact angle, particle size, and tensile strength increased and the water swell, viscosity, and elongation at break decreased when the dispersions were modified with PMMA via the PU macroiniferter technique.

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