

PREPARATION AND CHARACTERIZATION OF WATERBORNE POLYURETHANES MODIFIED WITH BIS(3-(1-METHOXY-2-HYDROXY-PROPOXY)PROPYL) TERMINATED POLYSILOXANES*

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Abstract Polyurethanes (PU) were prepared using toluene diisocyanate, polypropylene glycol, ethylene glycol, dimethylolpropionic acid and triethylamine, and a siloxane modified PU (PSU) was obtained through reaction of the PU prepolymers with bis(3-(1-methoxy-2-hydroxypropoxy)propyl) terminated polysiloxanes (PMTS) of different molecular weight, specifically designed for this purpose. Results showed that, with increases in molecular weight of PMTS and its content, viscosity of the final PSU latexes decreased; phase separation of the incorporated PMTS in PSU films increased; the average particle sizes of the latexes varied between 110 nm and 330 nm, and the surface tension in the final latexes was relatively constant regardless of PMTS amount and its molecular weight. It was likely that copolymerized polysiloxanes had trend to enrich on top of the film when PMTS molecular weight was around 2000 and its content above 5 wt%. In general, PMTS modified polyurethane films showed higher performance than those from unmodified waterborne polyurethane latexes.

Keywords: Dihydroxyalkyl polysiloxane; Polyurethanes; Modification.

INTRODUCTION

Polyurethanes have been widely used in automobile paints, furniture and textile industries as well as in biomass foam incorporated with renewable raw materials^[1]. Waterborne polyurethanes (WPU), as nontoxic and nonflammable materials, have been abundantly used in a great variety of areas^[2]. However, compared to solvent based, WPU has shortcomings such as low water resistance and higher surface hydrophilicity. These shortcomings can be improved reportedly by incorporation of soft segments^[3]. It is well known that polysiloxanes (PSi) have interesting properties including low T_g , low surface energy, biocompatibility, high thermal and oxidative stability as well as good water resistance^[4]. Therefore, incorporation of PSi segments into WPU chains is expected to be effective to enhance WPU performance^[5–7]. Up to date, there are mainly three types of PSi used in polyurethane modification, *i.e.* PSi with hydroxyl function^[8–10], aminoalkyl function^[11–13] and hydroxyalkyl function^[14–16]. Difunctional polysiloxanes are often used for the synthesis of PSi-PU block copolymers, particularly difunctional hydroxyalkyl-containing polysiloxanes. Dihydroxy propoxyethyl terminated and dihydroxyhexyl terminated polysiloxane oligomers have been used for this purpose^[17]. In earlier studies, we have studied influence of ingredients in water-based polyurethane-acrylic hybrid latexes on latex properties^[18] and reported WPU modification with dihydroxypropyl terminated polysiloxanes^[19]. We also

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prepared and fully characterized bis(3-(1-methoxy-2-hydroxy propoxy) propyl) terminated polysiloxanes (PMTS)^[20]. In this report, PMTS is used in order to achieve polysiloxane modified anionic waterborne polyurethanes. The properties of the latexes and their films were studied.

EXPERIMENTAL

Materials

Polypropylene glycols (PPG) 210 and 220 (Third Petrochemicals of Tianjin, China), dimethylolpropionic acid (DMPA) (USA Trimet Product), ethylene glycol (Yanshan Petrochemicals, Beijing, China), PMTS (self-made^[20]) were vacuum-dried at 60°C for 2 h. Toluene diisocyanate (TDI, Yinguang Chemicals, Gansu, China) and diethylene triamine (Beijing Yili Chemicals, China) were used as received. Triethylamine (Guangcheng Chemicals, Tianjin, China) and acetone (Taixing Chemicals, Tianjin, China) were immersed in 0.5 nm molecular sieves for more than 1 week before use.

Preparation of Polysiloxane Modified Polyurethane Latexes and Their Films

The anionic PMTS-modified polyurethane latexes were prepared using TDI, PPG, DMPA, ethylene glycol, PMTS and triethylamine by acetone process. For the preparation of sample PSU1 (Table 1), 2.93 g (0.002 mol) of PMTS and 19.16 g (0.11 mol) of TDI were first charged into a reactor and heated to 70°C, then kept for 0.5 h. 9.00 g (0.009 mol) of PPG 210 ($M_n = 1000$) and 18.00 g (0.009 mol) of PPG 220 ($M_n = 2000$) were then added to the mixture and allowed to react for 0.5 h. 3.89 g (0.029 mol) of DMPA was then added to the mixture at 70°C followed by addition of 1.74 g (0.028 mol) of ethylene glycol. The mixture was kept at 70°C for 0.5 h to obtain the NCO-terminated prepolymers. The NCO value was determined using a standard dibutylamine back-titration method^[21]. The prepolymers were then cooled to 30°C. 40 g of acetone was added and stirred until prepolymers were dissolved followed by adding 2.93 g (0.029 mol) of triethylamine for neutralization.

Aqueous dispersions were obtained by adding the acetone solution of prepolymers, under high speed stirring, into 150 g of water containing diethylenetriamine, of which the amount was calculated based on residual NCO groups in prepolymer determined just prior to the dispersion preparation. The chain-extension reaction was allowed to proceed at 50°C for 2 h, and acetone was removed by evaporation. The resulting dispersion, denoted as PSU, had a solid content of 23 wt%–28 wt%. PSU latexes using PMTS of different molecular weights and at different levels were prepared following the same process. For preparation of PMTS-free WPU, 10.00 g PPG 210 and 20.00 g PPG 220 were charged. The other ingredients were kept unchanged. Films were cast from latexes on a Teflon plate at room temperature followed by drying at 60°C for 24 h. Molecular weight of all PMTS was estimated using GPC, NMR and chemical titration of the hydroxyl group^[20]. Here presented are the data from the chemical titration, which gave the results closer to expected values than the other methods.

Characterization of PSU and WPU Latexes and Their Films

Particle size and size distribution were measured using a Nano ZS light scattering instrument (Malvern, UK) at 25°C. Viscosity and surface tension of the latexes were determined at room temperature using spindle 3# at 30 r/min by RVDV-II+ viscometer (Brookfield, USA) and a JK99B automatic surface tension apparatus (Zhongchen, Shanghai, China).

The fractured section pictures of films were taken with a JSM-6700F field emission scanning electron microscope (SEM; JEOL, Japan). The tensile strength and elongation at break of the films were determined by an Instron testing machine (Instron Model 5569, USA). The films were stamped using a standard die, and tested at room temperature using a crosshead speed of 10 cm/min. The Shore hardness of the films was measured at room temperature by using an LX-A rubber durometer (Jiangdu, China). The TGA curves of the films were recorded on a Pyris Diamond TG/DTA (Perkin Elmer, USA) under nitrogen atmosphere from 30°C to 500°C at a heating rate of 10 K/min. The water and toluene absorption measurement of the films was carried out as follows: a preweighed dry slab (m_1) was immersed in water or toluene. After equilibration for 24 h, the sample was taken out and the excess liquid was wiped off using a Kleenex, and then the sample was weighed again (m_2). The water or toluene absorption is expressed as the weight percentage of water or toluene in the swollen sample: Water or toluene absorption (wt%) = $(m_2 - m_1)/m_1 \times 100$.

RESULTS AND DISCUSSION

Characterization of PSU and WPU Latexes

It is found that all latexes, either modified with PMTS or not, were all stable over 1 year standing at room temperature. For PU modification with polysiloxane, two sets of experiments were done as displayed in Table 1. In one set, the PMTS molecular weight was varied while keeping PMTS levels at 5 wt% (PSU1 to PSU5) relative to the total polymer; in another set, PMTS levels were changed while keeping molecular weight of PMTS constant at 1989 daltons (PSU2, PSU6 to PSU9). All data, including solids, viscosity, surface tension, particle size and dispersity index (PDI) of the latexes, are collected in Table 1.

Table 1. Formulation and properties of WPU and PSU latexes

Sample	M_n of PMTS	PMTS (wt%) ^a	Solids (wt%)	Viscosity (mPa·s)	Surface tension (mN/m)	Particle size (nm)	PDI ^b
WPU	0	0	26.49	1270	42.1	134.5	0.464
PSU1	1508	5.0	22.48	1140	44.9	325.1	0.543
PSU2	1989	5.0	27.11	1130	40.6	128.6	0.464
PSU3	2607	5.0	25.90	907	38.7	111.8	0.557
PSU4	2884	5.0	26.58	463	40.8	183.3	0.480
PSU5	3481	5.0	27.40	1600	44.1	144.7	0.682
PSU6	1989	2.5	26.40	787	43.2	121.0	0.657
PSU7	1989	7.5	27.64	590	41.2	133.7	0.467
PSU8	1989	10.0	26.90	137	35.2	114.6	0.538
PSU9	1989	12.5	27.03	47	31.7	199.1	0.806

^a PMTS wt% by weight with regard to all monomers;

^b Particle size dispersity index, PDI = 0 for monodisperse latex particles

It is clearly seen that latex viscosity of modified PSU latexes is lower than that of WPU, and this viscosity is gradually decreasing with increase in PMTS molecular weight with one exception of PSU5, the highest molecular weight of PMTS. Knowing that a stoichiometric amount of PPG was taken out when PMTS was employed in order to keep NCO/OH constant, and that polymer chains with PMTS segments are more water repellent compared with PPG chains, this decrease in latex viscosity was not unexpected, because PMTS segments in latex particles would be more tightly packed up and less extended into surrounding aqueous phase than PPG segments, so that leading to a lower viscosity. When keeping molecular weight of incorporated PMTS constant at 1989 and varying PMTS levels (PSU2, PSU6 to PSU9), latex viscosity descended from 787 mPa·s to 47 mPa·s. This can be well explained based on the same mechanism when increasing PMTS molecular weight. As for PSU5, the higher viscosity observed might be an indication that a change in particle morphology has occurred. When molecular weight of PMTS increased to 3481, the highest among all PMTS used, phase separation of PMTS might occur, leading to formation of tiny particles, and by consequence, this would contribute to increase the viscosity in the latex. This was very conceivable due to the highest molecular weight of PMTS used in this sample preparation, leading to therefore a higher particle size distribution (PDI) in the latex particles as seen in Table 1. Another possibility may be due to a more extended carboxyl groups to the surrounding aqueous phase^[22]. The carboxylic groups, originated from DMPA and the only groups responsible for particle stabilization in this latex, were believed to be more extended into aqueous phase with higher PMTS amount, because incorporation of PMTS in the polymer chains would increase the incompatibility between the polymer main chains and the chain terminal carboxyl groups, which may constitute an additional driving force for the carboxyl groups to extend further into the surrounding water phase, on one hand; and on the other hand, the polymer chains become more flexible with more PMTS incorporated, which would also facilitate the extending of the carboxyl groups into water phase.

The surface tension in the latexes was relatively constant as long as PMTS content being kept at 7.5 wt% or lower (PSU1 to PSU7) regardless of PMTS molecular weight. A perceptible decrease was observed when PMTS

levels were higher than 7.5 wt% (PSU8, PSU9). This decrease in latex surface tension could be attributed to the formations of either extreme small or large particles when PTMS of high molecular weight was used in the latex preparation as afore mentioned.

The particle size in unmodified WPU latex was around 134 nm. For latexes modified with PMTS, average particle sizes varied between 110 nm and 134 nm for most of the samples. Nevertheless, in latexes prepared with PMTS of the lowest (PSU1) and the highest molecular weights (PSU4 and PSU5), and with highest PMTS content (PSU9 with 12.5 wt% PMTS), larger particles were observed. Particle formation and growth in emulsion polymerization are controlled by a number of experimental parameters. There was no regular variation observed in particles size with PTMS content and its molecular weight. In the present case, size distribution was either bimodal or trimodal, and no single distribution was observed as shown in Fig. 1. This rendered the analysis on size variation more difficult. It is also needed to point out that the particle sizes given in Table 1 were obtained from light scattering, only a number average value was given. Particle size obtained this way was hydrated because of the hydrophilic groups on the surface of the particles.

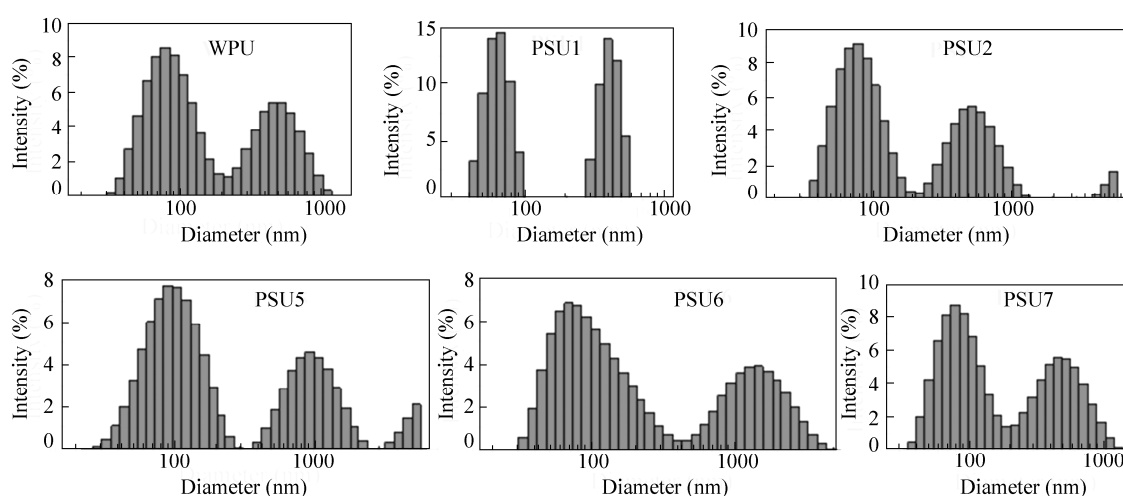


Fig. 1 Particle distribution histograms of latexes WPU, PSU1, PSU2 and PSU5–PSU7

Properties of PSU and WPU Films

Table 2 presents properties of WPU and PSU latex films. Pure polyurethane latex film was transparent. In contrast, all PMTS containing films were opaque except the two samples: PSU1 with 5 wt% PMTS of the lowest molecular weight, and PSU6 with the lowest PMTS (2.5 wt%) incorporated. This strongly suggests that the microstructure in these films kept the same as that in no-modified PU film, and no separated microdomains of PMTS were presented either when PMTS was copolymerized at low level (2.5 wt% in PSU6) or when PMTS of low molecular weight was used (PSU1) at 5 wt%. For the rest of the samples, where higher amounts of PMTS or/and PMTS of higher molecular weights were used, all latex films became opaque, which indicated that microdomains consisting of PMTS might be present, owing to very probably increased incompatibility between PMTS and PU chains.

As for the water and toluene adsorption of the latex films, it is believed that the polysiloxane segments of PMTS would be enriched on the surface of the latex films during late stage of film formation, because their water affinity is lower than that of PU chains. This has been also reported in literatures^[23, 24]. Hill *et al.*^[24] prepared blends of PTMO (polytetramethyleneoxide) with PU and PDMS (polydimethylsiloxane) with PU in their study on surface structure and heat properties of membrane formation. Their results showed that the mechanical properties of the blends were enhanced and the polymer membrane was polysiloxane-rich in the surface layer, and the separation extent of the soft and hard phases widened significantly because of the incompatibility between the hard and soft segments and the low surface energies of PSi. This would lower water absorption once PMTS was used in the samples. Water adsorption was decreased in all the samples when PMTS

was inferior to 10%. Here again, irregularity was observed in samples with very high PMTS content ($> 10\%$), the water absorption in PSU8 and PSU9 was similar to or even higher than that of the pure WPU latex film. This decrease was much lessened for toluene adsorption, because polysiloxane chains are more repellent to water than to toluene.

Table 2. Properties of WPU and PSU latex films

Sample	Appearance	Hardness (Shore A)	Water absorption (wt%)	Toluene absorption (wt%)
WPU	Transparent	81.7	60.95	67.74
PSU1	Transparent	79.1	—	73.21
PSU2	Opaque	73.6	56.50	66.50
PSU3	Opaque	74.1	—	63.22
PSU4	Opaque	75.7	44.35	71.55
PSU5	Opaque	76.4	53.23	66.76
PSU6	Translucent	76.5	45.94	61.74
PSU7	Opaque	75.7	44.96	61.47
PSU8	Opaque	77.2	60.32	64.63
PSU9	Opaque	74.5	69.64	65.35

Morphology Characterization of the Latex Films

Figure 2 displays SEM pictures of the fractured section of the latex films with different PMTS molecular weight but constant PMTS level of 5 wt%. It is found that in PSU1, the film with the lowest PMTS molecular weight, the fractured section was very smooth, very similar to WPU (free of polysiloxane). However, small grits appeared in PSU3, and large blocks seemed significant in PSU4. On the same time, pores were also perceptible. These grits, blocks or pores must be due to formation of microdomains of polysiloxanes. Similar structure is clearly observable in Fig. 3, where SEM pictures of the fractured section of the latex films with different PMTS levels (at constant molecular weight of 1989) are displayed. In PSU6, the sample with the 2.5 wt% PMTS (the lowest level), the fractured section was continuous though not smooth; with increase in PMTS from 5 wt% (PSU2) to 10 wt% (PSU8), the fractured surface morphology evolution was obvious, large pores were present in PSU8. From Figs. 2 and 3, it was conducted that phase separation extended with increase in PMTS molecular weight and its content. It was very likely 5 wt% PMTS with molecular weight of around 2000 was the best option to get highest performance in this polysiloxane modified waterborne polyurethane.

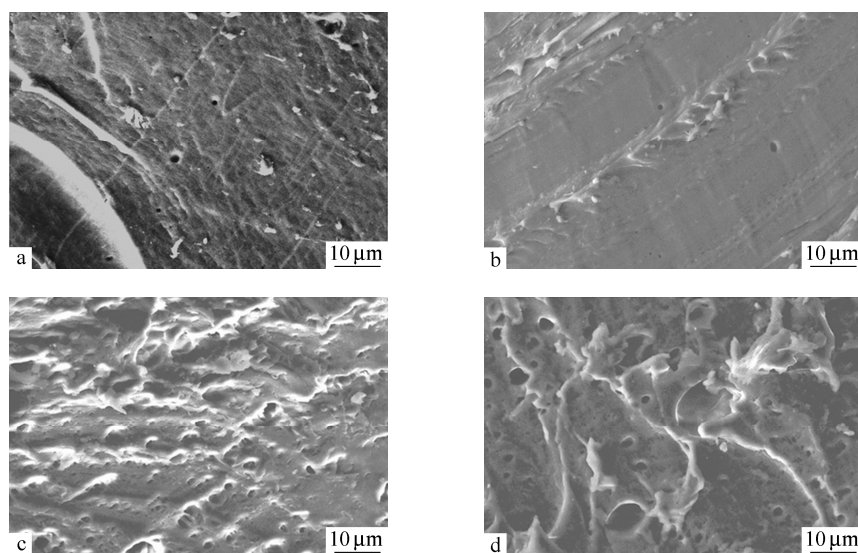


Fig. 2 SEM pictures of fractured film sections of (a) waterborne polyurethane (WPU) and those modified with PMTS polysiloxanes of different molecular weight (b) PSU1, 1508, (c) PSU3, 2607 and (d) PSU4, 2884

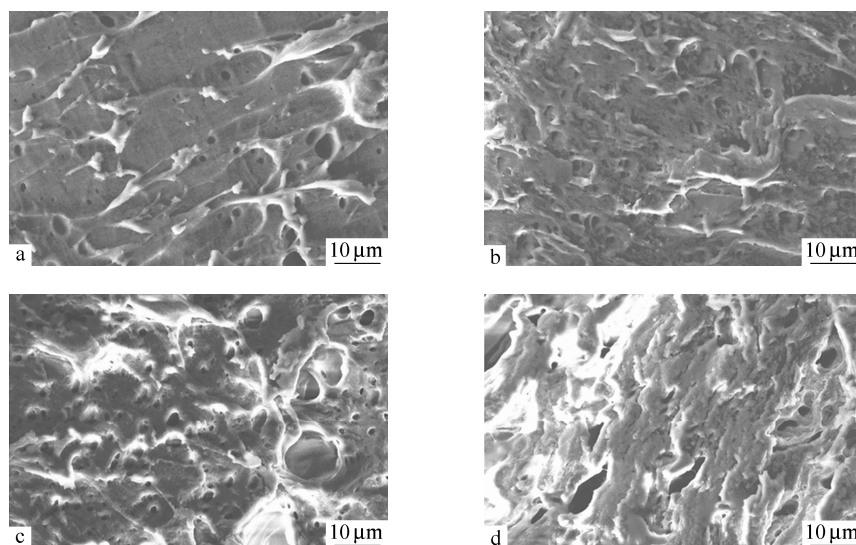


Fig. 3 SEM pictures of fractured film sections of waterborne polyurethane modified with PMTS polysiloxanes (molecular weight 1989) at varying content (a) PSU6, 2.5 wt%, (b) PSU2, 5.0 wt%, (c) PSU7, 7.5 wt% and (d) PSU8, 10.0 wt%

Mechanical and Thermal Properties of the Latex Films

The hardness of the PSU1 films was quite close to that of WPU (Table 2), it was slightly decreased in all tests of the samples with PMTS molecular weight above 1508 regardless of its content. This observation was in good agreement with the analysis that polysiloxanes tended to stay on the top of the films either when polysiloxane was blended^[24] or copolymerized with polyurethane^[25]. Presence or enriching of polysiloxane segments on the top of the films would surely contribute to reduce hardness of the films.

The influences of PMTS molecular weight on tensile strength and elongation of the films are shown in Fig. 4. It is seen that a maximum elongation (539%) appeared when PMTS molecular weight was 1989. While the tensile strength kept practically unchanged with PMTS molecular weight as long as it was below 2600; higher molecular weight of PMTS resulted in a gradual decrease in both the tensile strength and the elongation, which was readily attributed to eventual formation of microdomains of polysiloxane phase as discussed above.

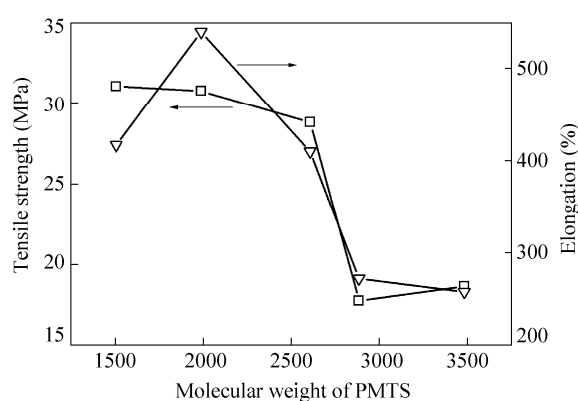


Fig. 4 Molecular weight of PMTS versus tensile strength and elongation

Taking the films with molecular weight of PMTS fixed at 1989, the effect of PMTS content on the tensile strength and elongation was studied. Figure 5 shows clearly that highest tensile strength and largest elongation were obtained with 5 wt% of PMTS; both tensile strength and elongation were weakened with higher and lower

PMTS levels, in comparison with the sample with 5 wt% of PMTS. These results demonstrated that PMTS amount and its molecular weight must be appropriate in order to obtain an optimization in the performance of the resulting materials. It was likely that the optimal mechanical properties were achieved when using PMTS of molecular weight at around 2000, and its content around 5 wt%.

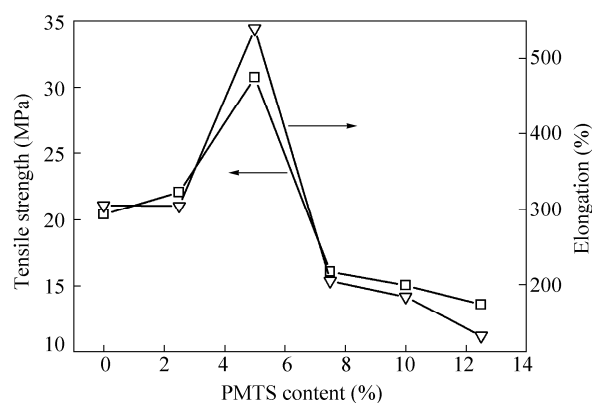


Fig. 5 PMTS content versus tensile strength and elongation

Figure 6 presents TGA curves of the latex films at different PMTS levels. It was seen that all samples possessed very similar profile in initial degradation up to 300°C. Significant differences between the samples were observed only beyond this temperature. By examining of these curves, it was found that thermal stability of the samples was closely related but not proportioned to their PMTS content. With 2.5 wt% PMTS (PSU6) the curve nearly overlapped with that of PMTS-free WPU (not given in Fig. 6); the thermal stability was enhanced with PMTS content up to 7.5 wt%, and then decreased with continuous increase in PMTS content. Therefore, latex film with 7.5 wt% of PMTS performed a high stability, followed by those with 5 wt% and 10 wt% of PMTS (not shown). Thermal stability of sample with 12.5 wt% of PMTS was inferior to the rest of the PMTS modified polyurethanes. This indicates that thermal stability was not only a simple function of PMTS content; it depended also on the microstructure or morphology of the materials. From above discussion, it was concluded that 5 wt% of PMTS being the optimum level for mechanical performance of the materials. When regarding the thermal stability, it seemed that sample with 7.5 wt% of PMTS performed better than that with 5 wt% of PMTS.

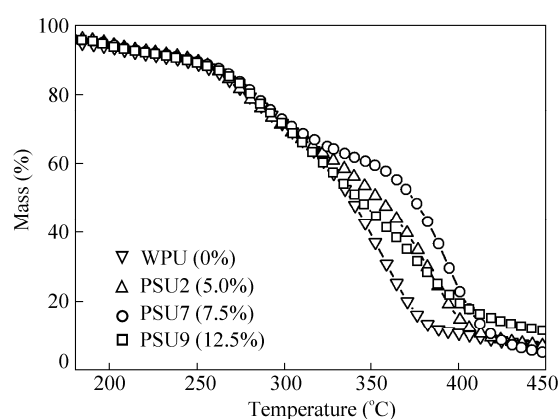


Fig. 6 TGA curves of PSU latex films with different PMTS content of same molecular weight 1989

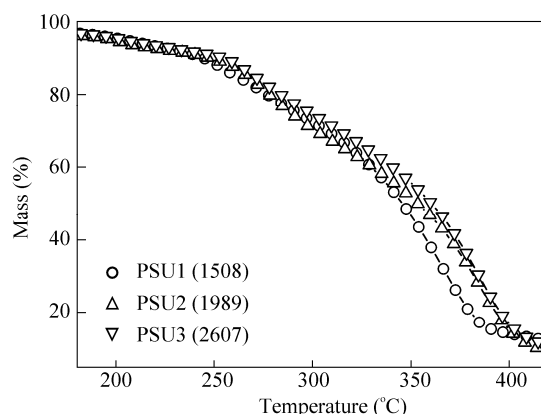


Fig. 7 TGA curves of PSU latex films with 5 wt% of PMTS of different molecular weight

In Fig. 7 are given TGA curves of the samples with 5 wt% PMTS but varying molecular weight of PMTS. This figure revealed that PSU3 with PMTS molecular weight of 2607 showed the best thermal stability, and followed by other samples in the adverse order of PMTS molecular weight. This enabled us to conclude that higher PMTS molecular weight contributed a better thermal stability providing appropriate PMTS content was used.

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