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Thermal degradation behaviors of poly (dimethylsiloxane)-urethane-graft-poly (methyl methacrylate) copolymers based on various diisocyanates

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The thermal decomposition behaviors of slightly crosslinked poly(dimethylsiloxane)-urethane-graft-poly(methyl methacrylate) (PDMS-urethane-g-PMMA) copolymers based on two diisocyanates: 2,4-toluene diisocyanate (2,4-TDI) and m-xylene diisocyanate (m-XDI) are discussed. By analyzing the residues of the decomposed copolymers and thermal degradation behaviors of copolymers, it was proposed that poly(dimethylsiloxane) (PDMS) in the copolymers traps free radicals generated from the thermal decomposition of the copolymer and reduces the rate of thermal decomposition. In addition, the crosslinking structure of PDMS can also reduce the evaporation of volatiles from the thermal decomposition process.

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1. Introduction

Thermal stability of poly(methyl methacrylate) (PMMA) is related to the polymerization mechanisms as has been reported by several researchers [1, 2]. If MMA was polymerized via free radical initiators, propagating chains may be terminated through disproportion, combination or chain-transfer reactions. The head-to-head linkages formed by the combination reactions may be degraded at 175°C. The production of unsaturated end groups by disproportionation reactions, and random scission within PMMA will be occur at 250°C and 360°C, respectively. All of these degradation steps result in weight losses of PMMA and can be determined by TGA.

In order to enhance the thermal stability of PMMA prepared by free radical polymerization, coupling a thermally stable polymer with PMMA is a valid method. Like other polysiloxanes, poly(dimethylsiloxane) (PDMS) exhibits excellent thermal and oxidative stability [3–6]. PMMA copolymers containing PDMS oligomers are prepared by the macromonomer technique in this study [7–10].

In our previous study [11], the compatibility and impact resistance behaviors of slightly crosslinked poly (dimethylsiloxane)-urethane-graft-poly(methyl methacrylate) (PDMS-urethane-g-PMMA) copolymers based on two diisocyanates: 2,4-toluene diisocyanate (2,4-TDI) and m-xylene diisocyanate (m-XDI) have been discussed. This paper focuses on the thermal stability of these copolymers and attempts to investigate how the PDMS-urethane segments attach to the PMMA main chains of the copolymers and affect the thermal stability of the copolymers.

2. Experimental

2.1. Materials

Poly(dimethylsiloxane)-α, ω-diol (PDMS-diol) (trade name: X-22-160-AS) was obtained from Shin-Etsu Chemical Co., Japan. The molecular weight of PDMS is 1037 determined by quantitatively analyzing the hydroxyl groups of PDMS. m-Xylene diisocyanate (m-XDI) 2,4-toluene diisocyanate (2,4-TDI), and hydroquinone were purchased from Tokyo Chemical Industry Co., Japan. Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), anhydrous methanol and benzene were recervied from Aldrich Chemical Co., U.S.A. Stannous octoate and azobisisobutyronitrile (AIBN) were purchased from Lancaster Synthesis Company U.S.A. and Showa Chemical Co. Japan, respectively. PDMS-diol was dried under vacuum at 60°C for 6 hours. MMA and HEMA were purified by vacuum distillation. Other reactants and reagents were used as received.

2.2. Synthesis of macromonomers

Two types of PDMS-urethane macromonomers based on 2,4-TDI and m-XDI were synthesized by adding a two molar amount of PDMS-diol with 0.15 wt%

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stannous octoate into benzene solution containing 10 wt% m-XDI or 2,4-TDI and stirring at 60°C in a dry atmosphere. When the absorption peak of the hydroxyl group in the IR spectra disappeared, an equi-molar amount of methanol and HEMA containing 1 wt% hydroquinone were added into the mixture and the temperature was kept below 60°C to prevent thermal polymerization. When the absorption peak of the isocyanate group at 2270 cm^{-1} in the IR spectra was absent, the reaction was considered to be completed. The contaminants were removed from the reaction mixture by decolorizing carbon and the solvent was evaporated by vacuum distillation. The products were characterized by IR, GPC and NMR [11]. The codes PRETDI and PREXDI are used to be present the PDMS-urethane macromonomers based on 2,4-TDI and m-XDI, respectively.

2.3. Synthesis of PDMS-urethane-graft-PMMA copolymer

The PDMS-urethane macromonomers and MMA monomers were mixed and were copolymerized by adding 0.3 wt% AIBN at 60°C in nitrogen atmosphere. As the viscosity of the reaction mixture was raised rapidly, it was cooled down to room temperature and was transferred to a mold formed by two sheets of glass. The copolymerization was conducted at 60°C for 12 hours and 90°C for 3 hours. Pure PMMA specimen was synthesized by the same method without macromonomers. Pure PDMS-urethane homopolymer was synthesized by the same method without MMA monomer.

In this study, the symbols of SiTY, SiXY are used to represent the copolymer, where Si is the siloxane monomer, T is 2,4-TDI, X is m-XDI and Y is the content of diisocyanate in phr unit (i.e. part per hundred parts of copolymer). For instance, SiT22.5 represents the copolymers based on 22.5 phr 2,4-TDI macromolecules [11]. The PDMS-urethane homopolymers with two diisocyanates: m-XDI and 2,4-TDI are termed PDMS-XDI and PDMS-TDI, respectively. On the other hand, the blends based on homogeneous PMMA and 20 phr PDMS-urethane homopolymers are referred as to XDI-blend and TDI-blend, respectively.

The thermal degradation characteristics of pure PMMA, blends and copolymers in m-XDI and 2,4-TDI systems were determined using a TA 951-thermogravimetric analyzer, under nitrogen atmosphere at a heating rate of 10°C/min.

3. Results and discussion

The silicon-oxygen bond of PDMS has a high energy of dissociation 451.4 kJ/mol, as compared with 357.4 kJ/mol for carbon-carbon bonds [12, 13]. Therefore, the thermal stability of the copolymer can be improved by increasing the amount of PDMS-urethane macromonomers in the copolymer. The PDMS-urethane macromonomers are copolymerized with MMA monomers and become the side chains of the copolymer. The thermal degradation characteristics of homogeneous PMMA chains depend on the polymerization mechanisms. Thus, it is reasonable to investigate the effect of PDMS-urethane side chains in the copolymer on the thermal stability of the PDMS-urethane-g-PMMA copolymer.

TABLE I 5% and 10% weight loss temperatures (°C) of neat PMMA and copolymers

	PMMA	SiT7.5	SiT15	SiT22.5
5%weight loss	283	298	310.5	321
10%weight loss	323	333	344.5	351
	PMMA	SiX7.5	SiX15	SiX22.5
5%weight loss	283	304.5	306	324
10%weight loss	323	337.5	345	351

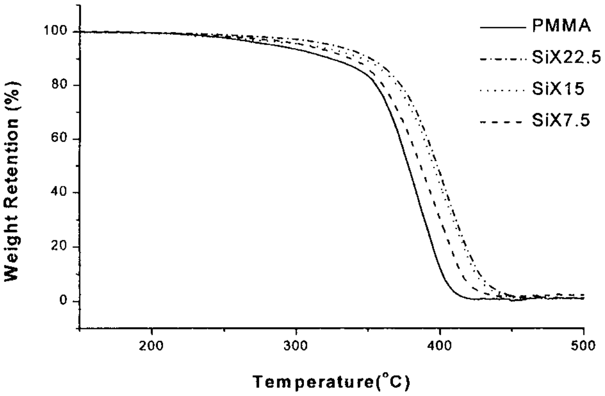

Figure 1 Thermogravimetric analysis of PMMA and copolymers in m-XDI system.

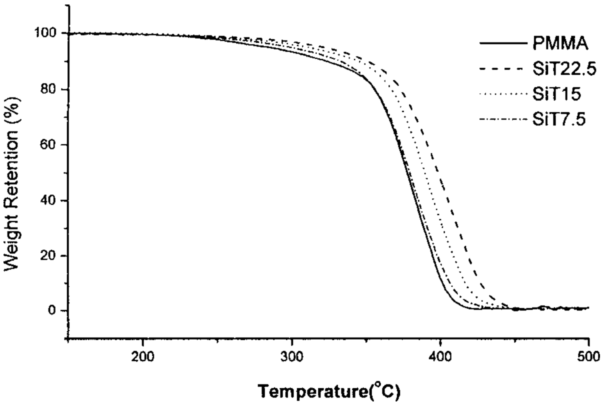

Figure 2 Thermogravimetric analysis of PMMA and copolymers in 2, 4-TDI system.

The thermal degradation characteristics of copolymers in m-XDI and 2,4-TDI systems are illustrated in Figs 1 and 2 by TGA under nitrogen atmosphere. Although the onset of weight loss of pure PMMA and copolymers are the same at approximately 180°C, the curves of weight retention of the copolymers extend to the higher temperature zone. Furthermore, the pyrolyzed-volatiles of the copolymer decrease with the increasing PDMS-urethane macromonomer content in the copolymer at lower temperatures. The thermal degradation behaviors of copolymers in m-XDI and 2,4-TDI systems are similar. Table I lists the temperatures of 5 wt% and 10 wt% weight loss of pure

PMMA and copolymers in the two systems. When PDMS-urethane macromonomer content in copolymers is 22.5 phr, the temperatures of 5 wt% and 10 wt% weight losses increase approximately 38°C and 41°C for SiT22.5 and SiX22.5 copolymers, respectively. From these observations, it is clear that all copolymers exhibit better thermal stability than pure PMMA and the thermal stability of these copolymers are dependent on the PDMS-urethane macromonomer content.

In order to discuss the effect of PDMS-urethane macromonomer on the thermal degradation behaviors of the copolymers, the TGA curves of homogeneous PMMA, PDMS-urethane homopolymers, PMMA/PDMS-urethane blends and copolymers based on m-XDI and 2,4-TDI systems were measured and the results are shown in Figs 3 and 4. Figs 5 and 6 show the derivative weight loss curves for m-XDI and 2,4-TDI systems, respectively.

In this paper, the PDMS-urethane homopolymers with two diisocyanates: m-XDI and 2,4-TDI are termed PDMS-XDI and PDMS-TDI, respectively. On the other hand, the blends based on homogeneous PMMA and 20 phr PDMS-urethane homopolymers are referred as to XDI-blend and TDI-blend, respectively. The results in Fig. 3 show that the weight loss of homogeneous PMMA is less significant before 180°C. In Fig. 5, the peak of the derivative weight loss curve of homogeneous PMMA for "head-to-head" scission around 175°C is not obvious. The weight loss is distinct beyond 200°C and two peaks of derivative weight loss curve appear at 246°C (the weight loss of unsaturated end-group of PMMA) and 370°C (the weight loss due to random segment scission), respectively [1].

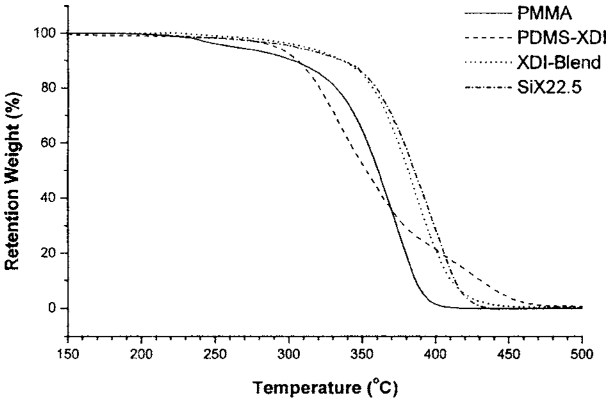

Figure 3 Thermogravimetric analysis of PMMA, PDMS-XDI, XDI-Blend and SiX22.5.

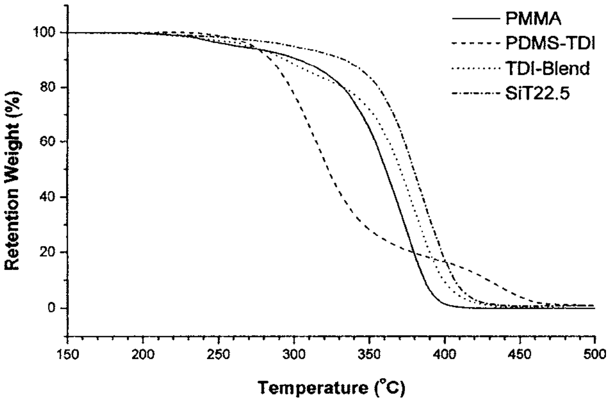

Figure 4 Thermogravimetric analysis of PMMA, PDMS-TDI, TDI-Blend and SiT22.5.

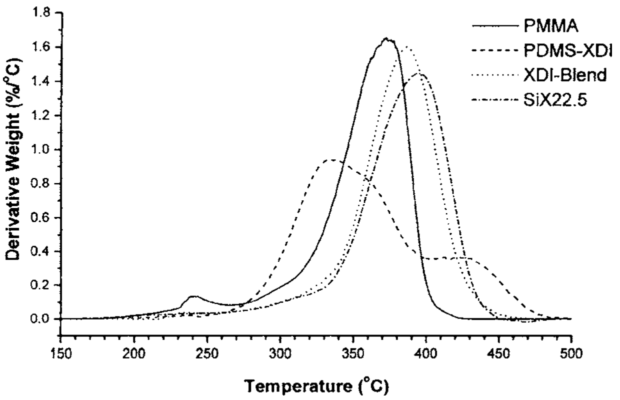

Figure 5 Derivative weight loss curves of PMMA, PDMS-XDI, XDI-Blend and SiX22.5.

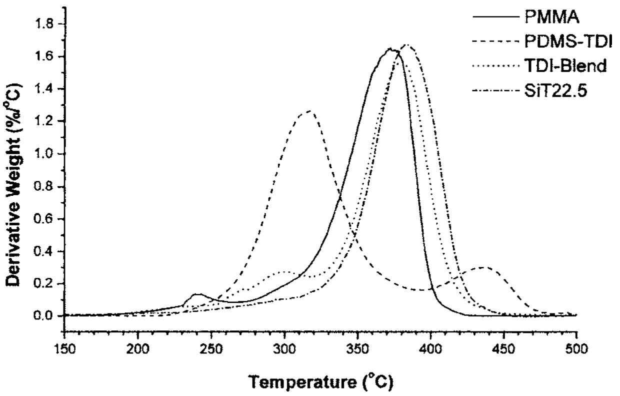

Figure 6 Derivative weight loss curves of PMMA, PDMS-TDI, TDI-Blend and SiT22.5.

There are three possible paths for polymer radicals generated from chain scission at the head-to-head linkages by thermal degradation: (1) polymer radicals generated to form MMA monomer during the depolymerization process; (2) disproportionation termination of the radials initiated by the chain scission at the head-to-head linkages, due to cage effects under the expected high viscosity of the sample within the temperature range (165°C); (3) polymerization of monomers from unzipping with polymer radicals, since the ceiling temperature (197°C) is near or above the temperature range in which the weight loss occurs from the chain scission at the head-to-head linkages [1]. Path (1) causes weight loss of PMMA by evaporating MMA monomer; path (2) reduces the molecular weight of the polymer. However, path (3) increases the molecular weight of polymer.

In order to investigate the pyrolysis path of head-to-head linkages, homogeneous PMMA is preheated up to 200°C in nitrogen atmosphere. Molecular weights of original PMMA and preheated PMMA were measured by using GPC, results are shown in Fig. 7. The average number molecular weight (Mn) of original PMMA is 227,000 and that of preheated up to 200°C is 216,000, respectively. The average number molecular weight

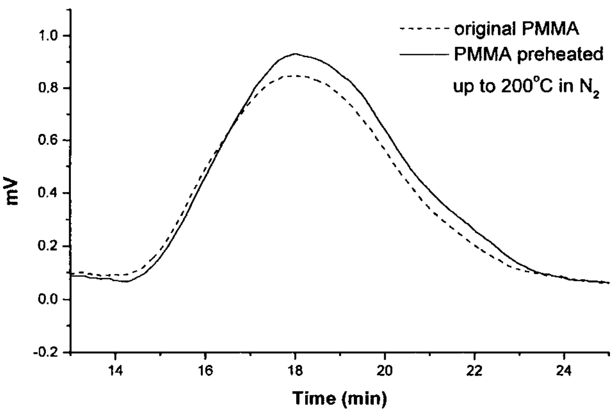

Figure 7 GPC curves of original PMMA and PMMA preheated up to 200°C in N_2.

(Mn) of PMMA preheated to 200°C decrease to 95% of the Mn of original PMMA. From this result, it is clear that the path (2) is the major pyrolysis path of head-to-head linkages in this study, however, the weight loss of homogeneous PMMA is not obvious at 180°C [15].

From Figs 3 and 5, it can be found that the thermal degradation of PDMS-XDI homopolymer starts at 250°C, and the thermal degradation process continues until 500°C. And the chain-scission of PDMS-XDI homopolymer initially occur at 280°C. The temperature of the maximum weight loss rate of PDMS-XDI homopolymer occurred at 330°C, which is lower than that of homogeneous PMMA (370°C). The initial thermal decomposition of PDMS-XDI homopolymer is that the PDMS-urethane side chain degrades [14, 15]. In addition, the temperature of the maximum weight loss rate of XDI-blend is shown at 383°C. Therefore, thermal stability of homogeneous PMMA is better than that of PDMS-XDI homopolymer, but worse than that of XDI-blend [14, 15]. From above data, thermal degradation behavior of XDI-blend is different with that of homogeneous PMMA and PDMS-XDI homopolymer. Therefore, it may conclude that homogeneous PMMA and PDMS-XDI homopolymer affect the thermal degradation behaviors of each other. Furthermore, the temperature of maximum weight loss rate of SiX22.5 copolymer is around 400°C and even higher than that of XDI-blend. The chemical bonding of copolymer between PDMS-urethane side chain and PMMA main chain improves the thermal stability of copolymers significantly.

From Figs 4 and 6, one can see the thermal stability of PDMS-TDI homopolymer is worse than that of PDMS-XDI homopolymer and homogeneous PMMA. Chain-scission of PDMS-TDI homopolymer initially occurred at 250°C. The temperature of the maximum weight loss rate of PDMS-TDI homopolymer occurred at 310°C. The initial thermal decomposition of PDMS-XDI (or PDMS-TDI) homopolymer is due to PDMS-urethane side chain degradation [14, 15]. The initial thermal decomposition of TDI-blend occurs at 300°C. However, the temperature of the maximum weight loss rate is about 380°C for TDI-blend, and is close to the result of XDI-blend pyrolysis. Therefore, thermal stability of homogeneous PMMA is better than that of PDMS-XDI homopolymer, but worse than that of the XDI-blend. From the above data, the thermal degradation behavior of the TDI-blend is different from that of homogeneous PMMA and PDMS-TDI homopolymer. Therefore, it may be concluded that homogeneous PMMA and PDMS-TDI homopolymer affect the thermal degradation behaviors of each other. Furthermore, the temperature of maximum weight loss rate of ST22.5 copolymer is around 400°C and even higher than that of the TDI-blend. The chemical bonding of copolymer between PDMS-urethane side chain and PMMA main chain improves the thermal stability of copolymers significantly.

Comparing Fig. 5 with Fig. 6, it is shown that the thermal degradation temperature of SiT22.5 copolymer is similar to that of SiX22.5 copolymer. According to these results, it is proposed that the effect of the types of diisocyanate on the thermal stability of PDMS-urethane-g-PMMA copolymers and blends is insignificant, although the structural difference in the diisocyanates does affect the thermal degradation of PDMS-urethane homopolymers. However, the existence of the PDMS dominates the thermal stability of PDMS-urethane-g-PMMA copolymers and blends. Furthermore, chemical bonding of copolymer between PDMS-urethane side chain and PMMA main chain can further raise the pyrolysis temperature of the copolymers.

The weight-loss behaviors of homogeneous PMMA, copolymers and blends in m-XDI and 2,4-TDI systems heated at 355°C for a long time in nitrogen atmosphere are shown in Figs 8 and 9. As the temperature rises to 355°C and keep constant, homogeneous PMMA

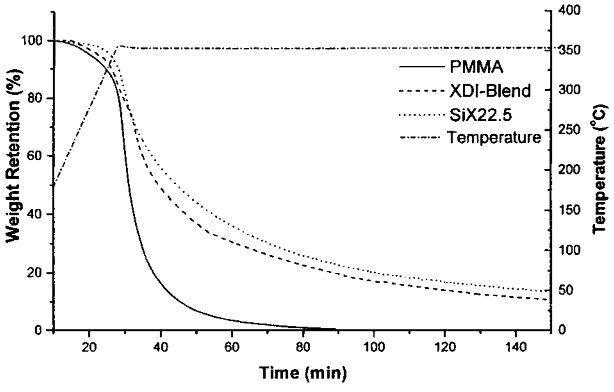

Figure 8 TGA curves of PMMA homopolymer, XDI-Blend and SiX22.5, which were heated to 355°C and kept isothermal for 2 hours.

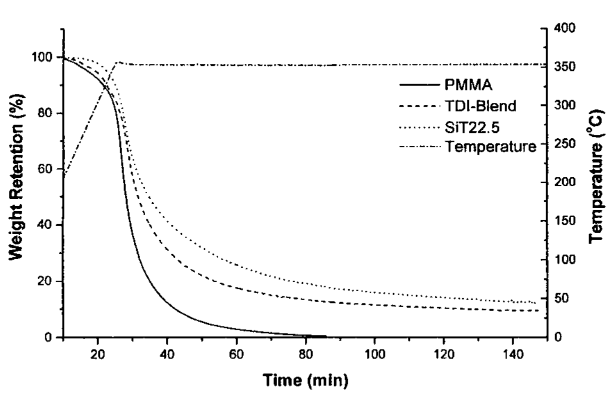

Figure 9 TGA curves of PMMA homopolymer, TDI-Blend and SiT22.5, which were heated to 355°C and kept isothermal for 2 hours.

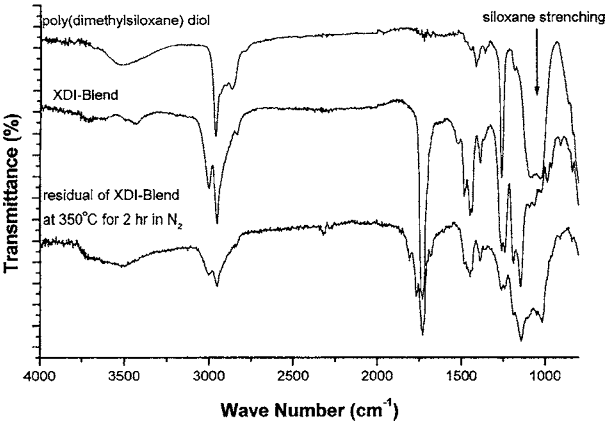

Figure 10 IR spectra of poly(dimethylsiloxane)-diol, XDI-Blend and residual of XDI-Blend.

remains evaporated and no residue, finally. However, the residual weight of XDI-blend is obviously decreased, and remains near 10 wt% after heating at 355°C for 2 hours. The weight loss curves of copolymers and blends change more moderately than that of homogeneous PMMA. Infrared spectra of residual XDI-blend show strong absorption of siloxane bands, comparing with XDI-blend in Fig. 10. Furthermore, the residual product just swells in THF. From these observations, the residue of XDI-blend is a crosslinked compound, mainly composed of siloxane. The pyrolysis of TDI-blend at 355°C is shown in Fig. 9, and the result is similar to that of XDI-blend.

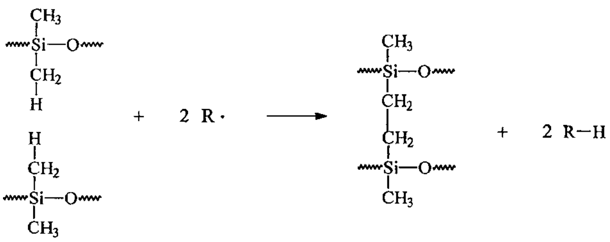

Figure 11 Crosslinking mechanism of poly(dimethylsiloxane) initiated by free radicals [1, 12–13].

TABLE II Swelling ratios of copolymers and molecular weights of PRETDI and PREXDI

	PRETDI		PREXDI	
Test Method	GPC	NMR	GPC	NMR
Mn	1593	1602 ^{a}(1547)	1776	1686.5 ^{a}(1575)
Mw	1768	–	2300	–
PDI	1.4685	–	1.2951	–
	SiT3.75	SiT22.5	SiX3.75	SiX22.5
Swelling ratio	4.157	3.268	5.883	3.721
Soluble fraction (wt%)	1.74	1.21	1.89	1.42

^{a}(): Theoretical value.

The role of PDMS on the thermal degradation process of PMMA-contained blends or copolymers can be distinguished. The thermal degradation of PMMA is a free radical depolymerization. PDMS degradation proceeds by a crosslinking reaction initiated by free radical attacking methyl groups on the PDMS and the radicals are consumed at high temperature (as shown in Fig. 11). PDMS in the copolymers can be considered as a PMMA-pyrolysis inhibitor and traps free radicals, which were generated from the thermal decomposition of the copolymer, and consequently, decelerates the thermal decomposition of blends or copolymers [1, 12, 13]. From the above results, thermal degradation of PMMA is mainly a main chain reaction in the copolymer and that of PDMS-urethane side chains in the copolymer proceeds urea crosslinking reaction below 350°C.

The surface morphology of residue generated from the copolymer-pyrolysis at 355°C in nitrogen atmosphere for 2 hours is shown in Fig. 12. It is different

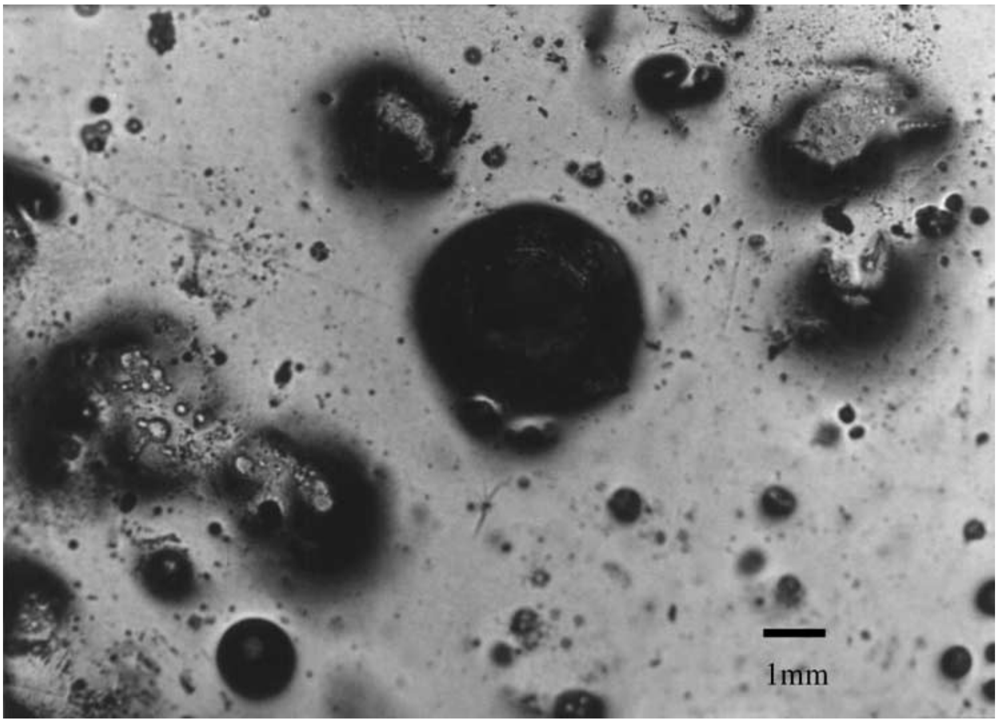

Figure 12 Optical microphotograph of surface morphology of the residue from thermally decomposed SiX22.5 copolymer (100×).

from the irregular appearance of residues of blends, which shows viscous flow during the thermal decomposition. The appearance of residues of copolymers is constant, except a lot of holes are spread on the surface of the residue as shown in Fig. 12. In our previous study [11], the copolymers have low crosslinking density from the results of swelling tests, as shown in Table II. Copolymer cannot flow as the initial thermal decomposition proceeds, and forms a crosslinked structure. Therefore, the volatiles from pyrolysis were trapped in the copolymer and could not be evaporated. As a result, the weight loss of crosslinking copolymers is decelerated, and even less than that of blends. Because the XDI-blend (or TDI-blend) consists of two linear polymers, the blend can flow when the temperature is higher than the glass transition temperature (T_g) of the blend. Therefore, the volatiles from pyrolysis evaporated, crosslinking reactions of PDMS cannot hinder the blend specimen flow. The internal violate of blends evaporate easier than that of copolymers. Hence, the thermal degradation curves of blends are lower than those for copolymers.

From above results, PDMS affects thermal stability of copolymers and blends. PDMS which attaches to the free radicals from the thermal decomposition of PMMA hinders depolymerization of free radicals from the thermal decomposition of PMMA, and reduces the rate of thermal decomposition of copolymers and blends. In addition, the crosslinking structure of PDMS can also reduce evaporation of volatiles from the thermal decomposition process.

4. Conclusion

In this study, the thermal decomposition behaviors of slightly crosslinked PDMS-urethane-graft-poly(methyl methacrylate) copolymers based on two difference diisocyanates: 2,4-toluene diisocyanate (2,4-TDI) and m-xylene diisocyanate (m-XDI) have been investigated. TGA results show that the thermal stability of copolymers in m-XDI and 2,4-TDI systems are all better than that of PMMA homopolymer.

The role of PDMS on the thermal degradation process of PMMA-containing alloys or copolymers can be distinguished by analyzing the residues of the decomposed copolymers and thermal degradation behaviors of copolymers. The thermal degradation of PMMA is a free radical depolymerization and PDMS degradation proceeds by a crosslinking reaction initiated by free radical attacking methyl groups on the PDMS, and the radicals are consumed at high temperature. Thus, it was proposed that PDMS in the copolymer traps free radicals which were generated from the thermal decomposition of the copolymer, and consequently, reduces the rate of thermal decomposition of copolymer. In addition, the crosslinked structure can also reduce the evaporation of volatiles from the thermal decomposition of the copolymer. The effect of the structural difference in the diisocyanates on the thermal decomposition of copolymers is less significant.

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