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Mechanical properties and hydrolytic stability of polyesterurethane elastomers with alkyl side groups

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Abstract

Polyester-based polyurethane elastomers with alkyl side groups were prepared from poly(adipate) glycols which involved 2,4-diethyl-pentamethylenediol or 3-methyl-pentamethylene diol as a novel glycol component and 1,5-pentamethylenediol. Segmented and allophanate-crosslinked polyurethane elastomers were prepared from these polymer glycols, 4,4′-diphenylmethane diisocyanate and 1,4-butanediol by a prepolymer method. Mechanical properties, dynamic viscoelastic properties, glass transition temperature (T_g), and thermal hydrolytic stability were measured. The properties of the polyurethane elastomers with alkyl side groups have good mechanical properties comparable to those of general purpose polyester urethanes. Novel polyester polyurethane elastomers with alkyl side groups had improved hydrothermal stability due to steric hindrance from hydrolysis of ester groups. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyurethane elastomers; Alkyl side groups; Hydrolytic stability

1. Introduction

Polyurethane elastomers (PUEs) have excellent mechanical properties compared with general purpose elastomers. These characteristics are utilized in a wide variety of industrial products, which are industrial parts, building materials, sports goods, medical equipment, adhesives and coatings. These properties are strongly dependent on not only chemical structure but also on superstructure of PUEs. However, PUEs are apparently much inferior to conventional rubber in their thermal stability, hydrolytic stability, and evolution of heat with dynamic deformation [1]. Properties of polyester-based PUEs are better than those of polyether-based PUEs, but hydrolytic stability is poor. Hydrolytic resistance of polyester-based PUEs has been improved by addition of carbodiimide compounds and use of polyester glycols with low concentration of ester groups, in which glycol components used are long hydrocarbon chains [1–3]. Hydrolysis of ester groups was studied by Newman, who found ‘Newman’s rule of six’ as an empirical rule [4]. Newman’s rule indicates that the greater the number of hydrogen atoms at the six position from carbonyl oxygen, the slower the rate of hydrolysis of ester groups. In our previous papers we have described relationships between structure and properties for the novel polyester-based PUEs with methyl side groups [5–9].

In this paper, segmented and allophanate-crosslinked polyurethane elastomers were prepared from poly(2,4-diethyl pentamethylene adipate) glycols or poly(3-methyl pentamethylene adipate) glycols. Mechanical properties and hydrothermal stability of these polyurethane elastomers were studied.

2. Experimental

2.1. Materials

Polyester glycols are poly(1,5-pentamethylene adipate)-glycol (PPA, Mn = 2015), poly(3-methyl-pentamethylene adipate)glycol (PMPA, Mn = 1966), and poly(2,4-diethyl-1,5-pentamethylene adipate)glycol (PDEPA, Mn = 1938). These polymer glycols were supplied courtesy of Kyowa Yuka Inc. Co. Ltd, Japan. These polymer glycols were dried by bubbling nitrogen gas under the vacuum prior to use. 4,4′-Diphenylmethane diisocyanate (MDI) was supplied by Nippon Polyurethane Ind. Co. Ltd. MDI was used as received. 1,4-Butanediol (BD) as a curing agent was purchased as special grade and purified by distillation prior to use. Fig. 1 shows the structure of these polymer glycols.

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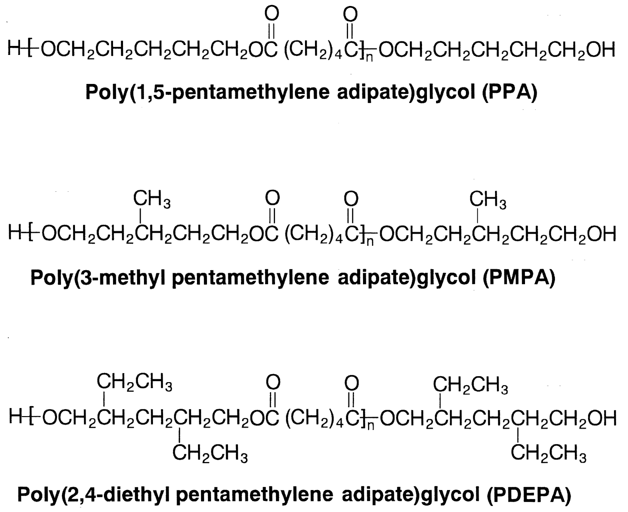

$$H\!-\!\!\left[OCH_2CH_2CH_2CH_2CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n\!\!-\!OCH_2CH_2CH_2CH_2CH_2OH$$

Poly(1,5-pentamethylene adipate)glycol (PPA)

$$H\!-\!\!\left[OCH_2CH_2\overset{CH_3}{\overset{|}{C}H}CH_2CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n\!\!-\!OCH_2CH_2\overset{CH_3}{\overset{|}{C}H}CH_2CH_2OH$$

Poly(3-methyl pentamethylene adipate)glycol (PMPA)

$$H\!-\!\!\left[OCH_2\underset{\underset{CH_2CH_3}{|}}{\overset{CH_2CH_3}{\overset{|}{C}H}}CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_2O\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\right]_n\!\!-\!OCH_2\overset{CH_2CH_3}{\overset{|}{C}H}CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_2OH$$

Poly(2,4-diethyl pentamethylene adipate)glycol (PDEPA)

Fig. 1. Structure of polyadipate glycols used.

2.2. Preparation of PUEs

Prepolymers were prepared from each polymer glycol and diisocyanate (K = [NCO]/[OH] = 3.0) at 80°C for about 3 h under a nitrogen atmosphere. The extent of the reaction was measured by an amine-equivalent method. The prepolymer and chain extender (M = [NCO]/[OH] = 1.05 and 1.50) were well mixed for 90 s, and then the viscous reaction product was poured into a mould heated at 130°C. The viscous product was cured for 24 h at 110°C. These PUEs obtained are abbreviated as follows: PPA-PUE, PMPA-PUE and PDEPA-PUE.

2.3. Measurements of properties

Density was determined by measuring the weight of the sample both in water and in air. Swelling behaviour was measured by a weighing method after equilibrium swelling in *N*,*N*-dimethyl acetamide (DMA) at 50°C. DSC thermograms of the PUEs were obtained by means of Seiko DSC-210 with workstation SSC 5200H (Seiko Co. Ltd, Japan) at a heating rate of 10°C/min from − 150°C to 250°C under a nitrogen atmosphere. The *FT*i.r. spectrometer, JASCO FT-IR-7000 (Japan), equipped with an attenuated total reflection (ATR) instrument at a resolution of 4 cm^{-1} at ambient temperature was used. Hardness was tested by a rubber hardness tester (Asker, Japan) based on the method described in ASTM D2240. Tensile tests were carried out

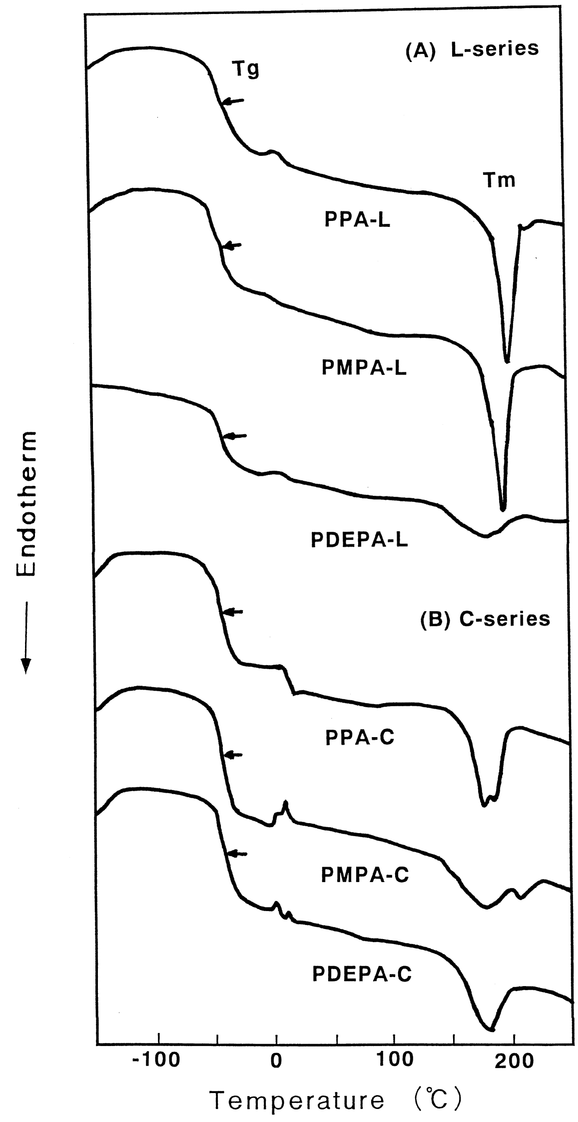

Fig. 2. DSC thermograms of polyadipate glycol-MDI-BD polyurethane elastomers.

Table 1
Formulation, structure parameter, and appearance of polyurethanes

Sample	Formulation MDI:-polyol:BD (molar ratio)	Gel fraction (%)	Density (g/cm^3)	Hardness (JIS-A)	T_gs	ΔT	Tm_h	Appearance
PPA-L	3.0:1.0:1.96	solble	1.23	80.5	− 33.8	19.3	201.7	yellowish, opaque, rubbery
PMPA-L	3.0:1.0:1.92	solble	1.19	78.4	− 38.6	13.3	195.4	yellowish, opaque, rubbery
PDEPA-L	3.0:1.0:1.92	solble	1.14	74.8	− 38.1	11.5	180.2	milky, opaque, rubbery
PPA-C	3.0:1.0:1.24	65	1.22	74.0	− 39.7	10.5	178.4	milky, opaque, rubbery
PMPA-C	3.0:1.0:1.32	18	1.17	72.5	− 39.9	10.5	180.2	yellowish, opaque, rubbery
PDEPA-C	3.0:1.0:1.28	25	1.15	72.3	− 36.3	10.5	182.1	milky, opaque, rubbery

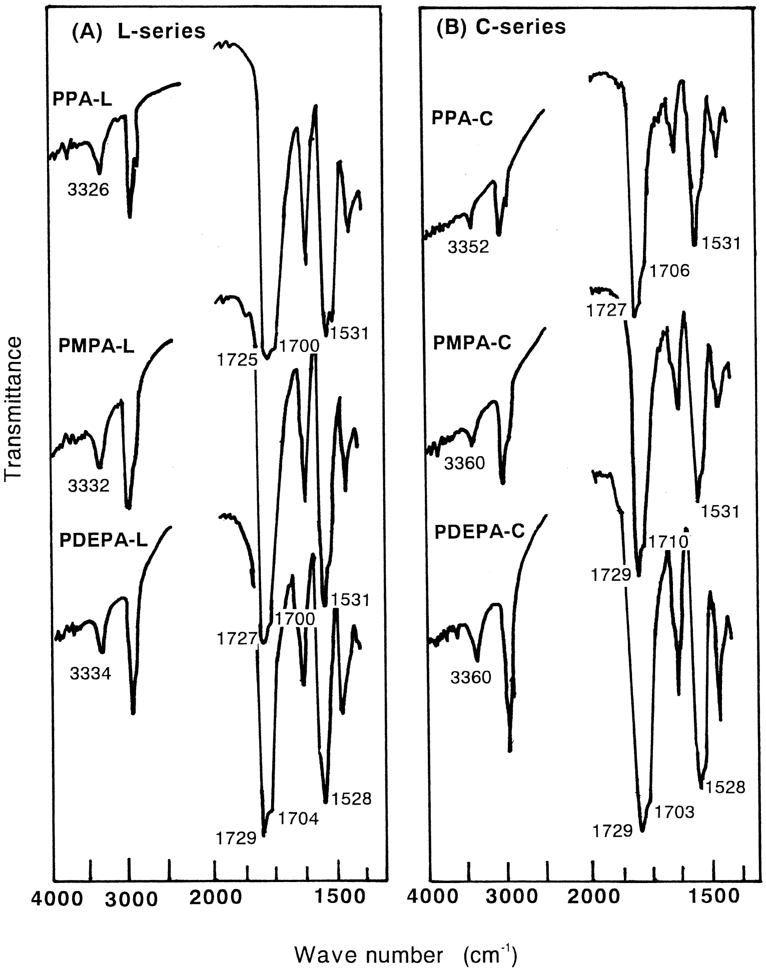

Fig. 3. *FT*i.r. spectra of polyadipate glycol-MDI-BD polyurethane elastomers.

with an Instron type tensile tester (Shimadzu AGS-100A, Japan) at a strain rate of 0.33/min at 30°C. Temperature dependence of dynamic mechanical properties was measured by using a Rehovibron DDV-IIC dynamic viscoelastometer (Orientec Co. Ltd, Japan) at an operating frequency of 110 Hz from − 150°C to 200°C at a heating rate of 2°C/min. Hydrolytic stability of PUEs were measured as follows: A rectangular specimen was cut, using a die, with a length of 40 mm and a width of 2 mm, and was immersed in water at 100°C. The sample was subjected to the tensile test at the required time. The tensile test was carried out with 15% elongation of the sample under the same conditions as those described previously.

3. Results

The formulation, some physical properties and appearance of PUEs prepared are shown in Table 1. In Table 1, details of -L and -C in mean linear PUEs and allophanate crosslinked PUEs are given. The appearance of all the PUEs was opaque and rubbery. L-series PUEs were soluble in DMA and each gel fraction of C-series PUEs was low. Density and hardness of these PUEs decreased with increasing size and the number of alkyl side group as follows: PPA- > PMPA- > PDEPA-. The density and hardness of each allophanate crosslinked PUE was lower than those of the corresponding L-PUE.

Fig. 2 shows DSC thermograms of L-series and C-series PUEs. While the glass transition temperature (T_g) of PPA-L was − 33.8°C, the T_g of PMPA-L and PDEPA-L with alkyl side groups was − 38.6°C and − 38.1°C respectively. In the crosslinked PUEs, the T_g of PPA-C, PMPA-C, and PDEPA-C was − 39.7°C, − 39.9°C, and − 36.3°C, respectively. T_g decreased by incorporating alkyl side groups and allophanate crosslinkages. The temperature range of glass transition of PPA-L PUE is 19.3°C, while those of PMPA-L and PDEPA-L PUEs are 13.3°C and 11.5°C respectively. The glass transition range decreased with the incorporation of alkyl side groups. As shown in Table 1, C-series PUEs had similar T_g and a narrow glass transition range. The temperature of the sharp endothermic peak at about 180°C–200°C is assigned to the melting point of the hard segment domain (Tm_h). The Tm_h for L-series PUEs was

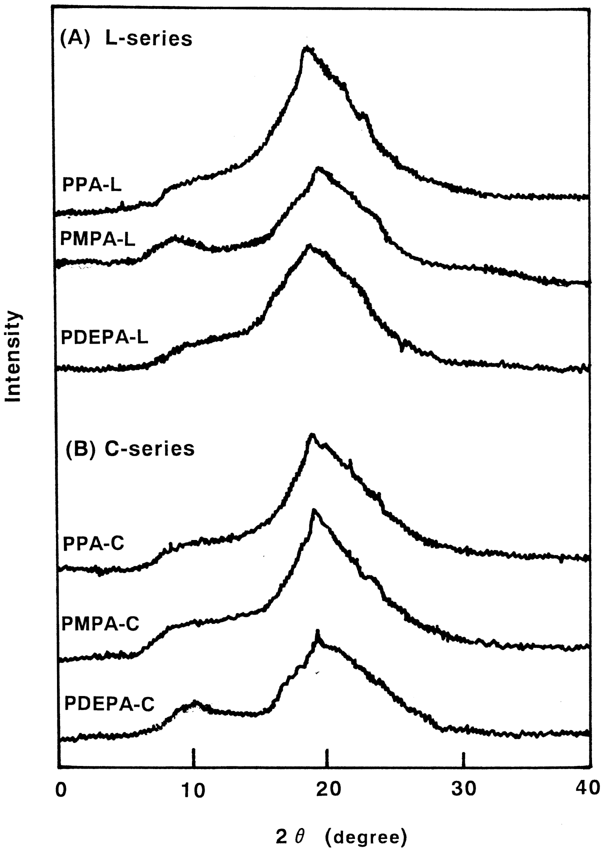

Fig. 4. X-ray diffraction profiles of polyadipate glycol-MDI-BD polyurethane elastomers.

201.7°C in PPA-L, 195.4°C in PMPA-L, and 180.2°C in PDEPA-L PUE. Tm_h of C-series PUEs was 178.4°C in PPA-C, 180.2°C in PMPA-C, and 182.1°C in PDEPA-C PUE. Tm_h also decreased with incorporation of alkyl side groups and crosslinks.

Fig. 3 shows *FT*i.r. spectra of NH– and C=O stretching range of the PUEs. NH stretching band assigned to hydrogen bonded NH groups was observed at 3326 cm^{-1} on PPA-PUE. This band shifted to 3332 cm^{-1} on PMPA-L, and 3334 cm^{-1} on DEPA-L PUEs. The wave number of hydrogen-bonded NH band increased with an increase in the number of alkyl side groups. C=O stretching bands of PPA-L PUEs were observed at 1725 cm^{-1} and 1700 cm^{-1}, assigned to non-bonded and bonded groups, respectively. These bands of PMPA-L and PDEPA-L PUEs with alkyl side groups were also at 1727 cm^{-1} and 1700 cm^{-1}, 1729 cm^{-1} and 1704 cm^{-1}. The peak intensity of the C=O$_{\text{free}}$ band on PPA-L PUE was much smaller than that of PUEs with alkyl side groups.

While the wave number of the hydrogen-bonded NH stretching band of C-series PUEs was increased up to 3352–3360 cm^{-1}, that of the non-bonded C=O stretching band was similar to that of L-series PUEs and bonded C=O bands had higher wave number than L-series PUEs. The frequency of NH + C=O bending bands at about 1530 cm^{-1} had similar values for all PUEs.

Fig. 4 shows wide angle X-ray diffraction profiles of PUEs. All diffraction patterns exhibit two broad peaks at approximately $2\theta = 10°$ and 20°. The peak at 10° indicates the existence of short-range ordering. Two small peaks at 20° and 25° were also observed in all samples. However, these peaks broaden by incorporating more alkyl side groups. These peaks correspond to three peaks at 18.2° (d = 4.92 Å), 22.9° (d = 3.88 Å) and 25.5° (d = 3.55 Å) observed in hard segment polymer (MDI/BD) [10,11].

Figs 5 and 6 show stress–strain curves and Mooney–Rivlin's plots. Mechanical properties are shown in Table 2. With incorporation of alkyl side groups, Young's modulus and tensile strength decreased and elongation at the break increased in linear type (L-series) PUEs. In the crosslinked PUEs (C-series), Young's modulus, tensile strength and elongation of crosslinked PUEs were increased more than for linear PUEs. In Table 2, $2C_1$ and $2C_2$ were determined as the intercept and slope from Mooney–Rivlin plots in Fig. 6. The value of $2C_1$ for L-series PUEs was about 1 MPa, but that of $2C_2$ for L-series decreased with incorporation of alkyl side groups. The value of $2C_1$ for C-series PUEs was about 1.5–1.0 MPa, but that of $2C_2$ changed from 2.7 MPa for PPA-C to about 1.3 MPa for PMPA-C and PDEPA-C.

Figs 7 and 8 show temperature dependence of dynamic mechanical properties of L- and C-series PUEs, respectively. In the L-series PUEs, the glass transition range of PMPA-L and PDEPA-L PUEs with alkyl side groups was narrower than PPA-L without alkyl side groups, and the slope of the former was higher. The storage modulus of the rubbery plateau decreased by incorporating alkyl side

Table 2
Mechanical properties of polyurethanes

Sample	Young's modulus (MPa)	σ_b (MPa)	ϵ_b	$2C_1$ (MPa)	$2C_2$ (MPa)
PPA-L	12.1	6.4	1.1	0.8	5.8
PMPA-L	9.6	6.6	2.5	1.2	2.6
PDEPA-L	8.8	7.4	2.9	1.4	1.5
PPA-C	10.4	14.1	3.6	1.3	2.4
PMPA-C	7.0	8.4	4.1	1.3	1.3
PDEPA-C	5.7	4.4	2.3	1.1	1.1

α_b: tensile strength, ϵ_b: strain at break, $2C_1$, $2C_2$: constant term of Money–Rivlin's equation

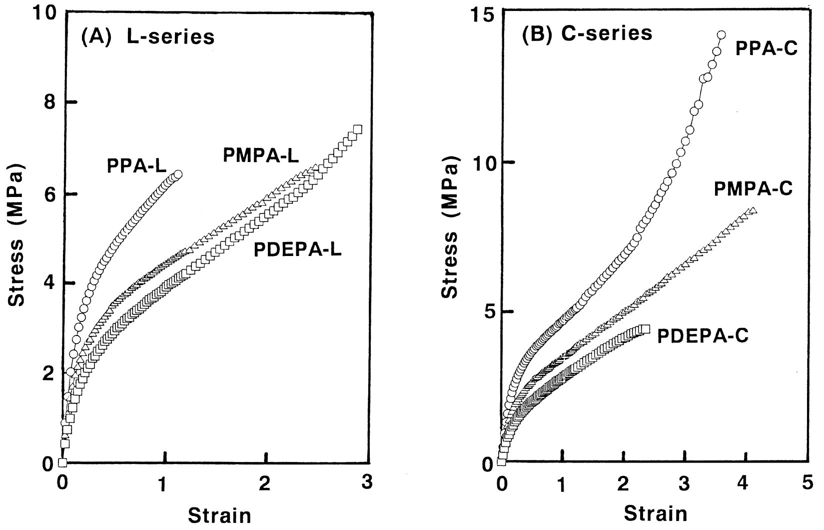

Fig. 5. Stress–strain curves of polyadipate glycol-MDI-BD polyurethane elastomers.

groups as follows: PPA-L > PMPA-L > PDEPA-L. The maximum temperature at which the rubbery plateau held constant was as follows: PPA-L 220°C, PMPA-L 200°C, PDEPA-L 190°C.

The temperature of E″max of L-series PUEs was as follows; PPA-L − 17.4°C, PMPA-L − 22.2°C, and PDEPA − 22.7°C. The change of temperature of tan δmax was also the same tendency as E″max. Peak intensity of α dispersion of each L-series PUE with methyl side groups was the same as that of PPA-L. A small peak (β dispersion) for all PUEs was observed near − 110°C in temperature dependence of E″.

On the other hand, the glass transition range of the C-series PUEs was 14°C. The storage modulus of the rubbery plateau of C-series PUEs did not differ by incorporating alkyl side groups. The maximum temperature at which the rubbery plateau held constant in PPA-C was 190°C, the same as that for PMPA-C and PDEPA-C. The temperature of tan δmax of C-series PUEs was also the same. The change in temperature of E″max also had the same tendency as tan δmax as follows: PMPA-C = PDEPA-C > PPA-C PUE. The peak intensity of α dispersion of C-series PUE with methyl side groups was the same as that of PPA-C PUE. The small peak (β relaxation) of all C-series PUEs was also observed near − 110°C in temperature dependence of E″.

Rectangular samples cut from PUE sheets were immersed in hot water at 100°C for 5 days. Fig. 9 shows relationships of the relative modulus with exposure time. The relative modulus of the all L-series PUEs decreased gradually. PMPA-L and PDEPA-L were more hydrothermally stable than PPA-L as shown in Fig. 9(A). The relative modulus of PMPA-C and PDEPA-C PUEs held their initial values up to 24 h and then the values decreased gradually, while the relative modulus of PPA-C decreased initially and this decrease became more significant with time, so that at 92 h the value was half of the initial modulus. The comparison of L-series with C-series PUEs indicated that

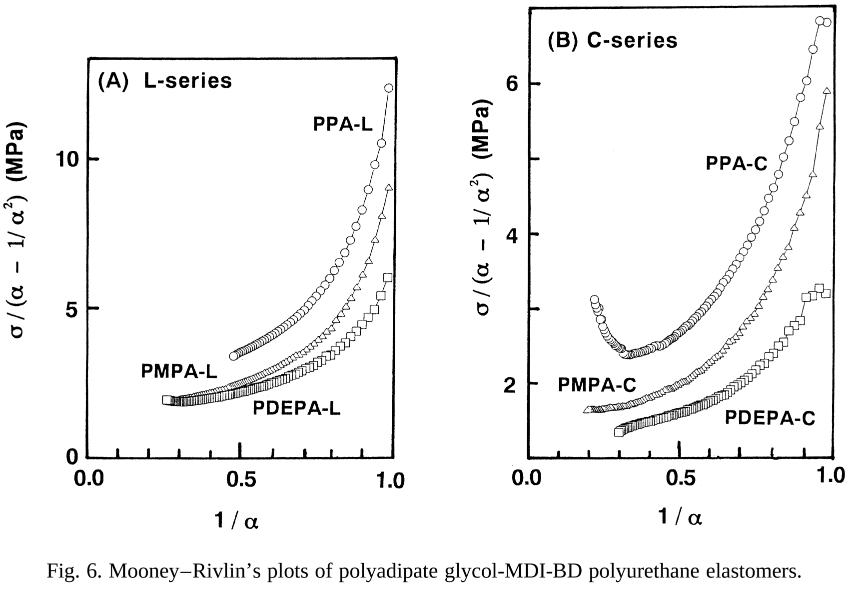

Fig. 6. Mooney–Rivlin's plots of polyadipate glycol-MDI-BD polyurethane elastomers.

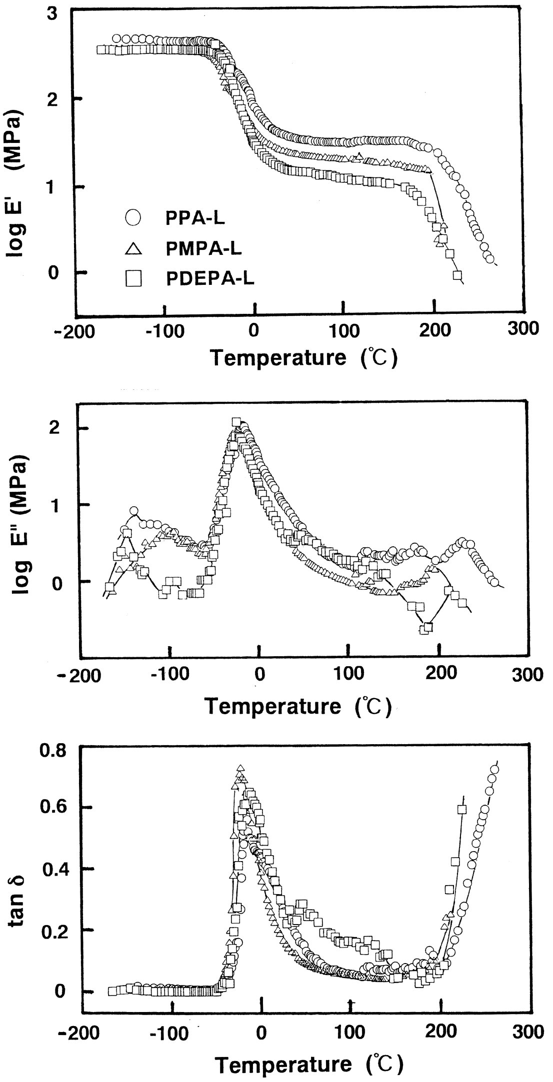

Fig. 7. Temperature dependence of dynamic mechanical properties of polyadipate glycol-MDI-BD segmented polyurethane elastomers.

thermal hydrolytic stability of L-series PUEs was better than C-series PUEs due to the addition of thermal decomposition of the allophanate crosslinks to ester hydrolysis of main chains.

4. Discussion

The novel polyester glycols (PDEPA and PMPA) are liquid polyester glycols which do not crystallize. PPA is a crystalline polyester glycol at ambient temperature. The decrease of density and hardness with the incorporation of alkyl side groups are attributed to a decrease in the crystallinity of soft segments. The decrease of density with incorporation of allophanate crosslinks is due to interference of the aggregation of hard segment chains. The lower glass transition temperature of L-series PUEs with alkyl side group than that of PPA-L is in agreement with the lower glass transition of the corresponding polyols. As shown in Fig. 2 and Table 2, high melting point and sharp peak intensity of hard segment domains in PPA-L and PMPA-L indicates that these PUEs have a high degree of microphase separation and PDEPA-L PUE have low microphase separation. Allophanate crosslinked PUEs decreased microphase separation introduced by crosslinks. Two peaks of PPA-C and PMPA-C PUEs from 150°C to 200°C shown in Fig. 2 suggest that these PUEs have two types of hard segment domains. Urethane groups of all these PUEs were hydrogen-bonded because NH stretching bands at 3450 cm^{-1} assigned to non-bonded NH were not observed in Fig. 3. The increase of the wave number of the hydrogen-bonded NH band and the C=O band with incorporation of alkyl side groups lead to a decrease in the strength of hydrogen bonding in PUEs with alkyl side groups. Introduction of crosslinks to PUEs also resulted in a decrease in the strength of hydrogen bonds. X-ray diffraction profiles in Fig. 4 show that the PUEs used are amorphous materials, and hard segment domains have weak crystallinity. These results show:

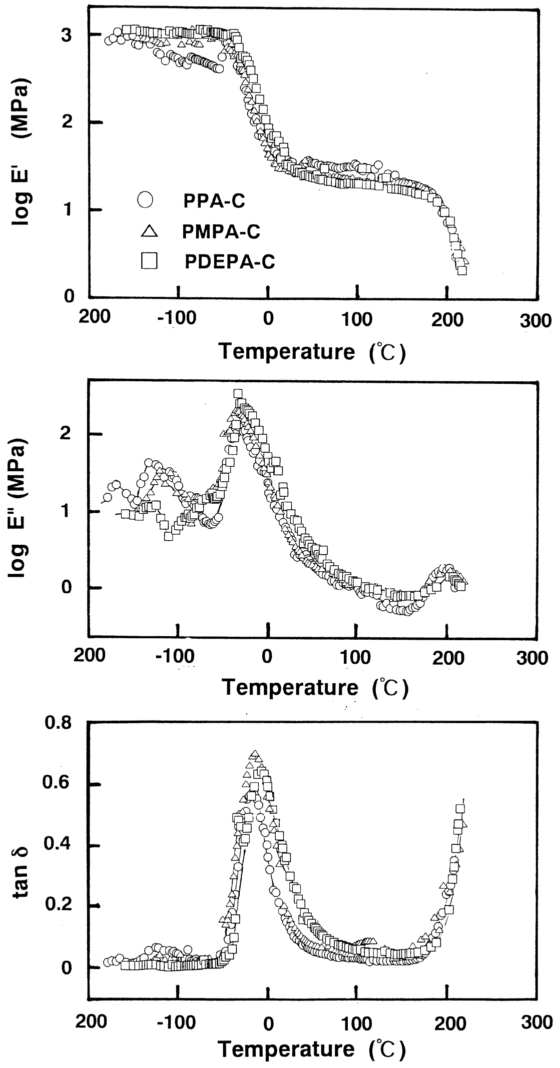

Fig. 8. Temperature dependence of dynamic mechanical properties of polyadipate glycol MDI-BD allophanate-crosslinked polyurethane elastomers.

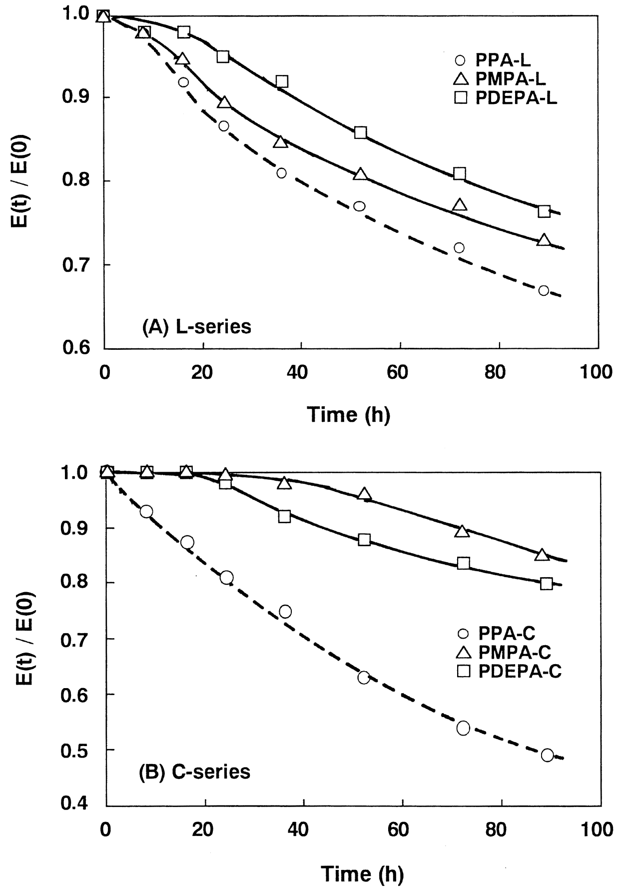

Fig. 9. Time dependence of hydrolytic stability of polyadipate glycol-MDI-BD polyurethane elastomers.

1. PPA-L PUE has a microphase separated morphology with strongly hydrogen-bonded hard segment domains.
2. PMPA-L with methyl side groups has a little microphase separated morphology.
3. PDEPA-L with ethyl side groups has mixed-phase morphology.
4. Introduction of allophante crosslinks progresses phase mixing.

Mechanical properties and thermal stability of the PUEs used are in the order of PDEPA-L < PMPA-L < PPA-L. These results are in agreement with the degree of phase separation and show that the reinforced filler effect of hard segment domains occurs. It is well known that tensile strength and modulus depend largely upon the presence of side groups in the polyesters; that is, polyesters containing alkyl side groups give elastomers a significantly lower modulus than linear PUEs. However, the novel PUEs with alkyl side groups give good mechanical properties. It is well known that $2C_1$ and $2C_2$ proportionate to concentration of chemical crosslinks and that of physical crosslinkages, respectively. Results shown in Table 2 suggest that the contribution of physical crosslinks to elastic modulus decreases with incorporation of alkyl side groups.

Fig. 9 shows that the novel PUEs with alkyl side groups have excellent hydrothermal stability. The apparent rate constant for hydrolysis was calculated by rewriting Fig. 9 according to chemorheological analysis of the following equation: $\ln E(t)/E(0) = A \exp(-kt)$ where $E(t)/E(0)$ is the relative modulus; k is the apparent rate constant for hydrolysis; and A is a constant. The apparent rate constant k (h^{-1}) obtained for each PUE is as follows: PPA-L 4.5×10^{-3}, PMPA-L 3.4×10^{-3}; PDEPA-L 3.2×10^{-3}; PPA-C 8.2×10^{-3}, PMPA-C 1.5×10^{-3}, PDEPA-C 2.6×10^{-3}. These results suggest that PDEPA-PUEs have the same hydrolytic stability as PMPA-PUEs. The good hydrolytic stability of the novel PUEs is ascribed to steric hindrance and electrostatic effects of alkyl side groups, which is illustrated by ‘Newman’s rule of six’ in which attack of reactive species to ester groups is easy or difficult as shown in Fig. 10.

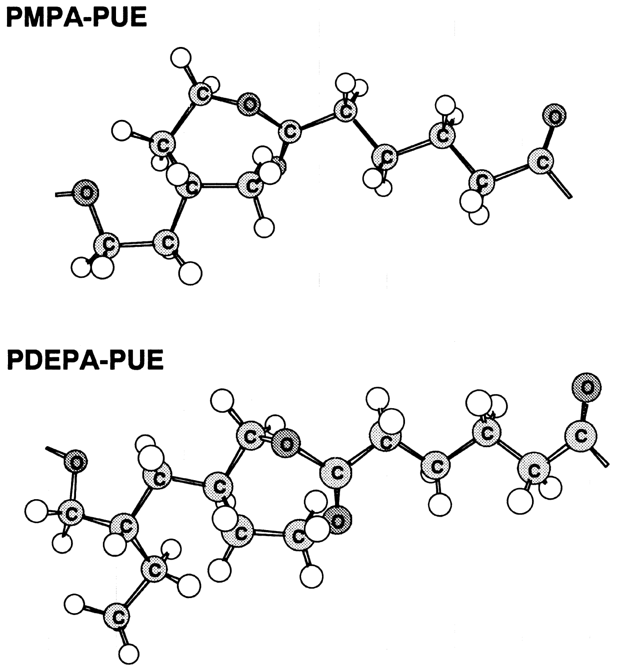

Fig. 10. Steric hindrance structure of PDEPA and PMPA chains for hydrolysis of ester groups.

5. Conclusion

Novel polyester glycols with alkyl side groups were used for the improvement of hydrothermal stability of polyester-urethane elastomers. The novel polyester glycols used were poly(2,4-diethyl-pentamethylene adipate)glycol (PDEPA) and poly(3-methyl pentamethylene adipate)glycol (PMPA). Novel polyurethane elastomers have good mechanical properties comparable to those of the general purpose polyester urethanes, and better hydrothermal stability. It is concluded that the introduction of methyl side and ethyl side groups to polyester chains according to the Newman’s principle [4] is an important procedure for improvement of the hydrolytic stability and weatherability of polyesterurethane elastomers.

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