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Microphase-separated structure and mechanical properties of novel polyurethane elastomers prepared with ether based diisocyanate

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Abstract

A diisocyanate baring ether bonds, 1,2-bis(isocyanate)ethoxyethane (TEGDI), was used for the preparation of polyurethane elastomers (PUEs). The PUEs were synthesized with either TEGDI or HDI, poly(oxytetramethylene) glycol (PTMG), and curing agents by a prepolymer method. 1,6-Hexamethylene diisocyanate (HDI) was also used as a control diisocyanate. The TEGDI-based PUEs exhibited highly softened property on account of flexibility of TEGDI itself and weaker phase separation. Another TEGDI-based PUEs were prepared with either poly(oxypropylene) glycol (PPG) or poly(caprolactone) glycol (PCL). Microphase-separated structure of these TEGDI-based PUEs are quite different from those with general diisocyanates and the PUEs were made be greatly softened.

Keywords: Polyurethanes; Microphase separation; Mechanical properties

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1. Introduction

Polyurethane elastomers (PUEs) have a lot of applications, because they can show quite interesting properties with a changing chemical structure of starting materials, molecular weight of polymer glycol, preparation conditions, and so on [1–11]. The PUEs are usually synthesized from polymer glycol, diisocyanate, and curing agent. Numerous starting materials have been used for the preparation of the PUEs to give them excellent properties. Hard segments possess a more different chemical nature than soft segments and separate into domains, which act as physical cross-links. Aggregation structure of the PUEs is well-known that it can be varied by changes of starting materials, hard segment content, degree of cross-linking, thermal history and so on.

The chemical structure of diisocyanate can be classified into two kinds. One is aromatic diisocyanate, and the other one is aliphatic one. The PUEs prepared with aliphatic diisocyanate have the feature that the PUEs obtained do not show the change of color by UV light and heat aging [12–14]. However, these PUEs with aliphatic diisocyanate, such as 1,6-hexamethylene diisocyanate, usually give hard materials because of its high crystallizability. Thus, the development of the aliphatic-based PUEs does not satisfy the demands in our life. Recently, the 1,2-bis(isocyanate)ethoxyethane (TEGDI) was synthesized to attain novel properties of polyurethanes [9]. This isocyanate has ether bonds in it. Since, ether groups have flexibility in comparison with a methylene chain, it is expected that the PUEs with this diisocyanate exhibit various properties that we have not attained.

In this study, we synthesized the poly(oxytetramethylene) glycol (PTMG)-based PUEs including either TEGDI or 1,6-hexamethylene diisocyanate (HDI) to understand the effect of the TEGDI on the microphase-separated structure and mechanical properties. We also prepared the TEGDI-based PUEs with poly(oxypropyrene) glycol (PPG) and poly(caprolactone) glycol (PCL), and shall clarify the general feature of the introduction of the TEGDI.

2. Experiment

Poly(oxytetramethylene) glycol (PTMG: $M_n = 2000$, Nippon Polyurethane Industry Co., Ltd, Japan), poly(caprolactone) glycol (PCL: $M_n = 2000$, Daicel Chemical Industry Co., Ltd, Japan) and poly(oxypropylene) glycol (PPG: $M_n = 2000$, Asahi Glass Co., Ltd, Japan) were used as a polymer glycol. A TEGDI (OCN–$(CH_2CH_2O)_2CH_2CH_2$–NCO, Nippon Polyurethane Industry, Co., Ltd, Japan), and 1,6-hexamethylene

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diisocyanate (HDI, OCN–$(CH_2)_6$–NCO, Nippon Polyurethane Industry Co., Ltd, Japan) were also employed as a diisocyanate. The purities of the diisocyanates were greater than 99%. A mixture of 1,4-butandiol (BD, Wako Chemical Co., Ltd, Japan) and 1,1,1-trimethylolpropane (TMP, Wako Chemical Co., Ltd, Japan) was used as a curing agent. The ratio of the mixture (BD and TMP) was 75/25 (w/w). The PUEs were synthesized by a prepolymer method. First, the polymer glycol was dried through dried nitrogen gas under a reduced pressure for ca. 4 h. The amount of residue water was confirmed with Karl Fischer titration. Prepolymers were prepared from dried polymer glycol and TEGDI or HDI with the ratios of $K=[NCO]/[OH]=3.0$ and 4.0 at 80 °C for 3 h under a nitrogen atmosphere. One drop of dibutyltin dilaurate (DBTL, Wako Chemical Co., Ltd, Japan) was added as a catalyst. The reaction was pursued by an amine equivalent method [15]. After finishing the reaction, the prepolymer was placed in a vacuum at 80 °C to remove the air involved inside. The prepolymer and curing agent were mixed well with the ratio of $[NCO]_{pre}/[OH]=1.05$ for 90 s, and the viscous product was poured into a mold constructed by a spacer of 2 mm thickness and two aluminium plates heated at 80 °C, where $[NCO]_{pre}$ is molar number of NCO groups in the prepolymers. The PUEs were demolded after 2 h curing, and then, they were postcured at 60 °C for 24 h in air.

To understand the crystalline structure of the hard segment chain in the PUEs, the regular polyurethanes were synthesized as a hard segment model. Samples were obtained by reacting either TEGDI or HDI and BD with $K=1$ at 70 °C. $-(TE–BD)_n-$ and $-(HD–BD)_n-$ denote the hard segment model sample of TEGDI and HDI.

The swelling behavior of the PUEs was investigated using benzene or *N*,*N*-dimethyl-acetamide (DMA). The PUEs were soaked in each solvent at 60 °C. The gel fraction, g, was defined as $g=W_b/W$, where W_b and W are the dried weight after swelling and original weight, respectively. The degree of swelling of the PUEs was determined from weight before and after equilibrium swelling with each solvent. The degree of swelling, q was defined as $q=1+\{(W_a-W_b)/d_s/(W_b/d_p)\}$. Here, W_a, d_s and d_p are the weight of sample swollen to equilibrium state, the density of solvent, and density of the PUEs, respectively.

Molecular arrangement of the PUEs was evaluated using wide angle X-ray diffraction (WAXD). WAXD profiles were obtained with a 2θ scan mode by a RINT2200 (Rigaku Co., Ltd, Japan). Voltage and current of an X-ray source were set to be 40 kV and 40 mA, respectively.

Differential scanning calorimetric (DSC) measurement was performed to understand the thermal behavior of the PUEs. DSC thermograms were obtained with a DSC (Rigaku DSC 8230, Rigaku Denki Co., Ltd, Japan) in the temperature range from −130 to 250 °C with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. As-prepared samples were simply cooled down around −140 °C, and then measurements were started.

Temperature dependence of dynamic viscoelastic properties was measured with a DMS 6100 (Seiko Instruments, Co., Ltd, Japan). The size of samples used is 25 mm × 5 mm × 2 mm. Measurements were performed in the temperature range from −150 to 250 °C with a heating rate of 2 °C min^{-1} in a nitrogen atmosphere. Imposed strain and frequency were set to be 0.2% and 10 Hz, respectively.

Tensile testing was performed with an Instron type tensile tester (Shimadzu, Autograph; AGS-100A, Japan) at 20 °C. The size of samples used is 60 mm × 5 mm × 2 mm. An initial length and elongation rate were set to be 15 mm and 5 mm min^{-1}, respectively.

3. Results and discussion

3.1. TEGDI- and HDI-based PTMG–PUEs

The TEGDI-based PUEs were compared with HDI-based ones because both diisocyanates possess six carbons and the HDI can be given as one the most popular diisocyanates. Appearances of the TEGDI- and HDI-based PTMG–PUEs were transparent and milky opaque, respectively. Table 1 shows density, gel fraction, and degree of swelling of the TEGDI- and HDI-based PTMG–PUEs with formulation ratios of $K=3$ and 4. The abbreviation of the PUEs denotes the kind

Table 1

Density, gel fraction, degree of swelling and mechanical properties of the TEGDI- and HDI-based PTMG–PUEs and PPG- and PCL-based TEGDI–PUEs with formulation of $K=[NCO]/[OH]=3$ and 4

Sample[a]	Molar ratio DI/polyol/BD/TMP	HSC/SSC[b] (wt%)	Gel fraction (%)		Degree of swelling		Density ($g\ cm^{-3}$)	Hardness (IHRD)	Young's modulus (MPa)	Tensile strength (MPa)	Strain at break (–)
			DMA	Benzene	DMA	Benzene					
PT–TE-3	3.0/1.0/1.4/0.3	28/72	90	93	4.4	5.2	1.06	55.8	2.0	10.2	6.1
PT–TE-4	4.0/1.0/2.2/0.5	34/66	97	98	2.7	1.6	1.06	57.4	2.4	5.5	4.4
PT–HD-3	3.0/1.0/1.5/0.3	25/75	83	97	6.0	3.7	1.05	85.4	7.4	14.1	3.3
PT–HD-4	4.0/1.0/2.2/0.5	32/68	98	100	3.1	2.3	1.08	88.8	14.3	16.6	3.4
PP–TE-3	3.0/1.0/1.3/0.3	28/72	93	95	5.9	5.8	1.04	35.2	0.8	1.4	4.1
PP–TE-4	4.0/1.0/2.1/0.5	34/66	84	84	9.0	9.1	1.10	33.5	0.8	1.0	5.8
PC–TE-3	3.0/1.0/1.3/0.3	25/75	97	97	4.7	3.3	1.16	86.6	11.2	31.9	4.6
PC–TE-4	4.0/1.0/2.1/0.5	35/65	96	98	4.9	2.8	1.14	84.4	10.3	42.3	5.8

[a] PT, PTMG; PP, PPG; PC, PCL; TE, TEGDI; HD, HDI.

[b] HSC, hard segment content; SSC, soft segment content.

of polymer glycol, isocyanate and K. PT, TE and HD denote PTMG, TEGDI and HDI, respectively. An obvious difference was not observed for the density of both PUEs. Gel fraction and degree of swelling of both PUEs with $K=3$ were larger and smaller than for $K=4$, respectively. This can be attributed to an increasing in hard segment content with stronger cohesion force. Hardness of the PT–HD-4 was larger than for the PT–HD-3, but those for the PT–TE-3 and -4 showed similar trends.

To evaluate the crystalline state of the hard segment modeles and the PUEs, WAXD measurement was carried out. Fig. 1 shows the WAXD profiles for the TEGDI- and HDI-based PTMG–PUEs with $K=3$ and 4 measured at 25 °C. WAXD profiles of the PT–TE-3 and PT–TE-4 exhibited only amorphous halo at around $2\theta=20°$. On the other hand, two small peaks in addition to an amorphous halo were observed at $2\theta=22.5$ and 24.0° for the PT–HD-3 and PT–HD-4. The intensity of these crystalline peaks for the PT–HD-4 was apparently larger than for the PT–HD-3. The WAXD profiles for these two hard segment models, $–(\text{TE–BD})_n–$ and $–(\text{HD–BD})_n–$, are also shown in Fig. 1. WAXD profiles for both model samples showed two crystalline peaks, indicating that the both hard segment chains are in a crystalline state at 25 °C. Peaks positions in these profiles were $2\theta=21.7$ and 22.9° for the $–(\text{TE–BD})_n–$ and 22.5 and 24.0° for the $–(\text{HD–BD})_n–$. Since, these peak positions of the $–(\text{HD–BD})_n–$ corresponded well to those obtained from the PT–HD-3 and PT–HD-4, it is likely to consider that two peaks are from the crystallized hard segment domains in the PUEs. These results clearly suggest that the HDI-based PUEs have crystalline hard segment domains in them. In contrast, although the $–(\text{TE–BD})_n–$ is in a crystalline state at 25 °C, they cannot crystallize in the TEGDI-based PUEs.

DSC measurement was performed to obtain the thermal properties of the PUEs. Fig. 2 shows the DSC thermograms for the TEGDI- and HDI-based PTMG–PUEs with $K=3$ and 4. Glass transition temperatures (T_gs) of the soft segment chains were observed at around −70 °C. Here, T_g of the original PTMG ($M_n=2000$) used in this study was −85 °C. T_gs of the soft segment in the TEGDI-based PTMG–PUEs were lower than those of the HDI ones. For the TEGDI-based PTMG–PUEs, unusual behaviors were observed. With an increasing temperature, strong exothermic and endothermic peaks because of crystallization due to rearrangement and melting of crystal of the soft segments were observed at around −30 and 18 °C, respectively. In contrast, the HDI-based PTMG–PUE did show only broad endothermic peak due to melting of the soft segment at around 5 °C. Also, the endothermic peaks due to the melting of the hard segment domain were observed at around 130 °C only for the PT–HD-3 and PT–HD-4. The reason that the PT–TE-3 and PT–TE-4 showed crystallization due to re-organization during heating process can be explained as follows. In the case of the general crystallizable PUEs like PT–HD-3 and PT–HD-4, the soft segment can be crystallized with cooling before DSC measurement because they have a microphase-separated structure; that is, each phase is composed of a rich phase. However, the soft segment in the PT–TE-3 and PT–TE-4 cannot be crystallized during the cooling process due to the presence of a large amount of the hard segment component in the soft segment phase. Therefore, it seems reasonable to conclude from WAXD and DSC that the HDI-based PUEs have a strong microphase separation, but the TEGDI-based ones do have a phase mixing trend.

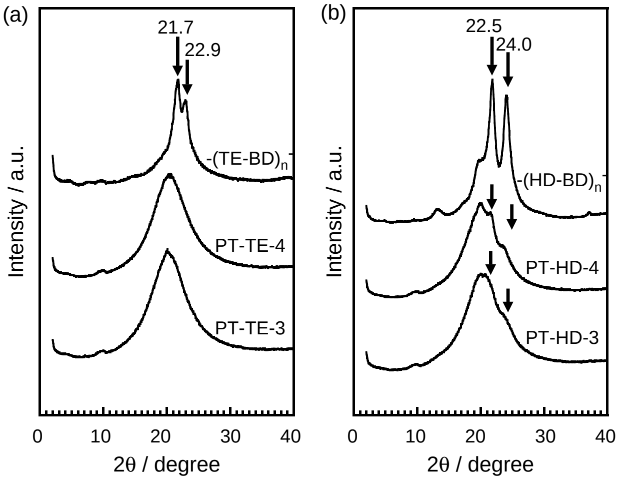

Fig. 1. WAXD profiles for the (a) TEGDI- and (b) HDI-based PTMG–PUEs with $K=3$ and 4 at 25 °C.

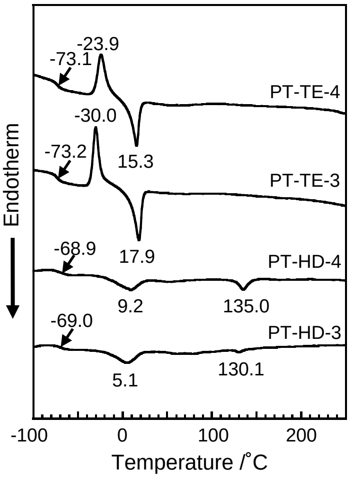

Fig. 2. DSC thermograms for the TEGDI- and HDI-based PTMG–PUEs with $K=3$ and 4. Heating rate was 10 °C min^{-1}.

We now have a discrepancy on T_g of the soft segment of the 'miscible' PUEs. Why is T_g of the soft segment in the TEGDI-based PUEs lower than that for the well phase-separated HDI-based PUEs? This seems to be explained as follows. Generally, an increasing T_g of the soft segment is observed when interacting with the hard segment with low mobility. However, in the case of the TEGDI-based PUEs, the mobility of the hard segment chains is not so low. Thus, even if the soft segments interact with NH bond of the hard segments, the molecular mobility of the soft segment will not be retarded so much. This might be the reason for this exceptional result.

Thermal and mechanical properties of the PUEs were investigated using dynamic viscoelastic measurement. Fig. 3 shows the temperature dependence of dynamic storage

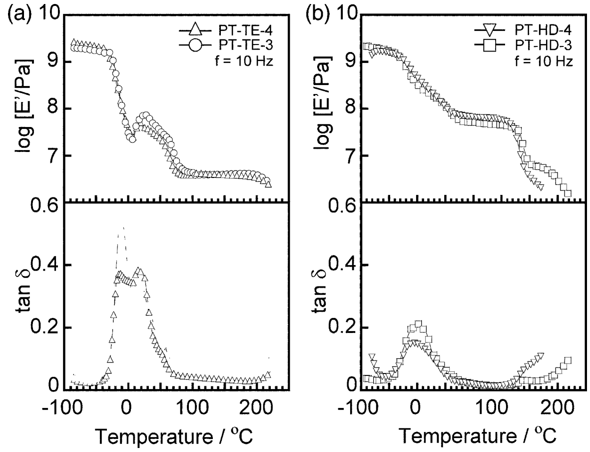

Fig. 3. Temperature dependence of storage modulus (E') and loss tangent (tan δ) for the (a) TEGDI- and (b) HDI-based PTMG–PUEs with $K=3$ and 4. Frequency of imposed strain and heating rate were 10 Hz and 2 °C min^{-1}.

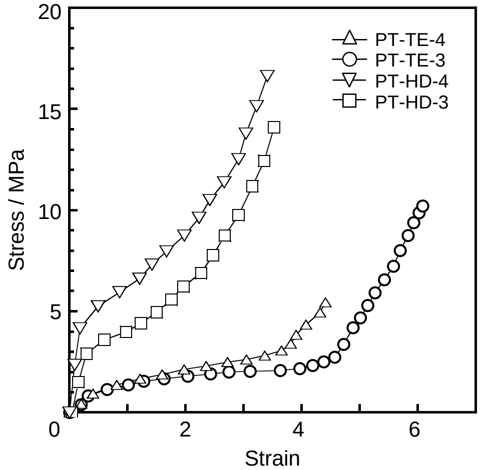

Fig. 4. Stress–strain curves for the TEGDI- and HDI-based PTMG–PUEs with $K=3$ and 4 at 25 °C.

modulus (E') and loss tangent (tan δ) for the TEGDI- and HDI-based PTMG–PUEs with $K=3$ and 4. During the heating process, E' of the PT–TE-3 and PT–TE-4 once increased at around room temperature due to recrystallization of the soft segment. Both PUEs exhibited rubbery plateau region above room temperature. The magnitude of E' around the rubbery plateau region for the PT–HD-4 was larger than for the PT–HD-3; on the other hand, both TEGDI-based PTMG–PUEs showed similar values. Also, the magnitude of E' for the TEGDI-based PTMG–PUEs was more than 1 decade smaller than the HDI-based PTMG–PUEs. This difference between the TEGDI- and HDI-based PTMG–PUEs will be discussed later with the results from tensile testing. In the tan δ curve, two peaks and a shoulder were observed for the PT–TE-3. They might be assigned to a glass transition, crystallization due to reorientation and melting of soft segment chain from lower temperature side. In the higher temperature region, a decreasing E' was obviously detected for the HDI-based PTMG–PUEs at around 140 °C, but not for the TEGDI-based PTMG-ones. This is because the melting of the hard segment domains occurred only for the HDI-based PTMG–PUEs as shown in Fig. 2.

Mechanical properties of the PUEs were investigated by tensile testing. Fig. 4 shows the stress–strain curves for the TEGDI- and HDI-based PTMG–PUEs with $K=3$ and 4 at 25 °C. The initial slopes of the PT–HD-3 and PT–HD-4 exhibited a high magnitude and then the increasing slope because of elongation-induced crystallization was subsequently observed, as usually observed for general elastomers. In contrast, the initial slopes of the PT–TE-3 and PT–TE-4 were quite small and stress kept low magnitude by strain, $\varepsilon=4$. Subsequently, increasing slope was observed at higher elongation region ($\varepsilon>4$). As shown in Table 1, Young's modulus, tensile strength and strain at break of the PT–TE-3 were 2.0 MPa, 10.2 MPa, and 6.1, respectively. Those magnitudes of the PT–HD-3 were 7.4 MPa, 14.1 MPa, and 3.3, respectively. That is, the TEGDI-based PUEs showed quite low Young's modulus and large elongation, indicating the TEGDI-based PTMG–PUEs are highly softened ones. As far as we know, this PUE can be classified as one of the most softened PUEs.

3.2. TEGDI-based PUEs with various polymer glycols

Next, we will discuss the aggregation structure and mechanical properties of the TEGDI-based PUEs with various polymer glycols. Generally, the PCL is a crystalline and biodegradable polymer glycols and gives high Young's modulus of the PUEs due to its crystallization. The PPG is an amorphous polymer glycol and gives low Young's modulus and elongation of the PUEs. Table 1 shows density, gel fraction, and degree of swelling of the PCL-, PPG- and PTMG-based TEGDI–PUEs with formulation ratios of $K=3$ and 4. Density and hardness of the PCL-based PUEs exhibited quite large number in comparison with PTMG- and PPG based PUEs due to the crystallinity of the PCL. Fig. 5 shows the WAXD profiles for the PCL-, PPG-, and PTMG-based TEGDI–PUEs with $K=3$ and 4 at 25 °C. No clear crystalline peak was observed for the PPG- and PTMG-based TEGDI–PUEs. These results suggest that both hard segment and soft segment components are in an amorphous state. The peak position and full width at half maximum (FWHM) of the amorphous halo of the PPG-based PUEs were smaller and larger than those for the PTMG ones, respectively. These are simply due to the side methyl groups of the PPG. In contrast, the strong crystalline peaks were observed at $2\theta=21.4$, 22.0 and 23.7° for the PCL-based TEGDI–PUEs with $K=3$ and 4. These peak positions correspond well to those from the PCL polymer glycol. Thus, it is conceivable that the PCL component in the PUEs is in a crystalline state at 25 °C.

Fig. 6 shows the DSC thermograms for the PCL-, PPG-, and PTMG-based TEGDI–PUEs with $K=3$ and 4. T_gs of the soft segment were observed around −74, −54, and −30 °C for the PTMG-, PPG-, and PCL-based TEGDI–PUEs, respectively. The PPG- and PTMG-based PUEs did not show any dependence of characteristic temperatures on K. In contrast,

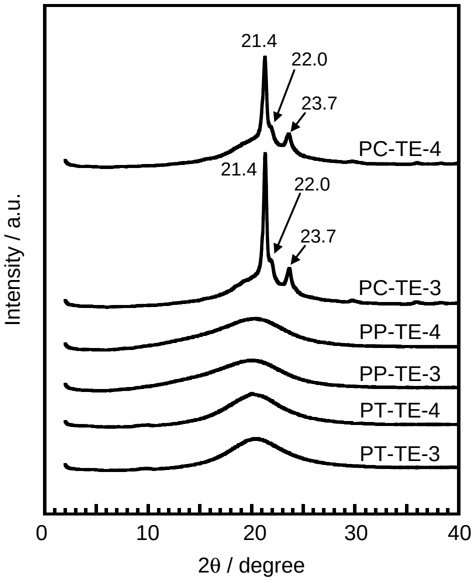

Fig. 5. WAXD profiles for the PCL-, PPG-, and PTMG-based TEGDI–PUEs with $K=3$ and 4 at 25 °C.

the T_g of the soft segment for the PCL-based PUEs increased with increasing K. For the PTMG- and PPG-based TEGDI–PUEs, glass transitions of the soft segment were clearly observed, but not for the PCL-based TEGDI–PUEs. However, the endothermic peak from melting of the crystallized PCL soft segment was obviously observed. The fact that the melting of the crystallized PCL chains was observed implies that the PCL crystallized without the hard segment components. In the other words, the soft segment and hard segment formed rich phases. Slight increasing T_g of the soft segment and decreasing melting point in the PCL-based PUEs suggest that the increasing interaction between soft segment and hard segment. On the contrary, since T_gs of original polymer glycols of the PTMG and PPG are -85 and -64 °C, respectively, the difference between T_g in the PUEs and T_g of original polymer glycol (ΔT_g) were calculated to be 12 and 11 °C, respectively. These numbers are quite small in comparison with other general PUEs. However, as stated in the previous section, no crystalline peaks in the WAXD profiles and endothermic peaks from crystallized hard segment domains. Hence, though the hard segment chains are dispersed in the soft segment phase, the molecular mobility of the soft segment was not affected by the interaction with the hard segment chains because of the high molecular mobility of the TEGDI-based hard segment chains.

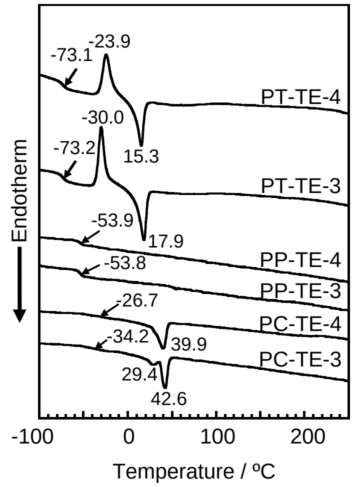

Fig. 6. DSC thermograms for the PCL-, PPG-, and PTMG-based TEGDI–PUEs with $K=3$ and 4. Heating rate was 10 °C min^{-1}.

Fig. 7 shows the temperature dependence of E' and tan δ for the PCL-, PPG- and PTMG-based TEGDI–PUEs with $K=3$ and 4. A starting temperature of decreasing E' and onset temperature of tan δ curves (-80 to -30 °C) showed similar magnitude compared with DSC results (Fig. 6). For the PTMG-based TEGDI–PUEs, E' decreased and once increased with an increasing temperature due to the recrystallization of the soft segment chain in the PUEs below room temperature, as mentioned in previous section. The E' of the PCL-based TEGDI–PUEs gradually decreased and tan δ curve showed broad peak in the temperature region (-50 to 50 °C). This is because the glass transition and melting of the crystallized soft segment chains occurred at around this temperature region. Changes in E' and tan δ curves of the PPG-based TEGDI–PUEs was the most abrupt of the three PUEs. The starting temperature of rubbery plateau region for the PPG-, PTMG- and PCL-based PUEs was around 0, 30 and 60 °C, respectively. This is because the PTMG and PCL are crystalline polymer glycols and they possess melting temperatures. The order magnitude of rubbery plateau region was as follows: PCL = PTMG > PPG. Since, PPG is quite flexible in comparison with PTMG and PCL, the magnitude of E' of the PPG-based TEGDI–PUEs exhibited fairly small magnitude of the three.

Fig. 8 shows the stress–strain curves for the PCL-, PPG- and PTMG-based TEGDI–PUEs with $K=3$ and 4 at 25 °C. The Young's modulus and tensile strength of the PCL-based TEGDI–PUEs showed the largest magnitude of the three on account of crystallization of the PCL component. And the PPG-based TEGDI–PUEs showed smaller Young's modulus

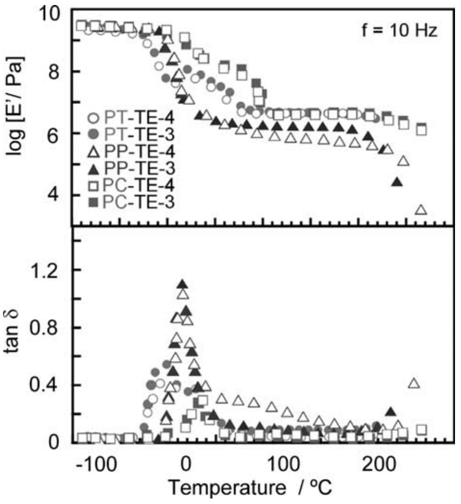

Fig. 7. Temperature dependence of E' and tan δ for the PCL-, PPG- and PTMG-based TEGDI–PUEs with $K=3$ and 4. Frequency of imposed strain and heating rate were 10 Hz and 2 °C min^{-1}.

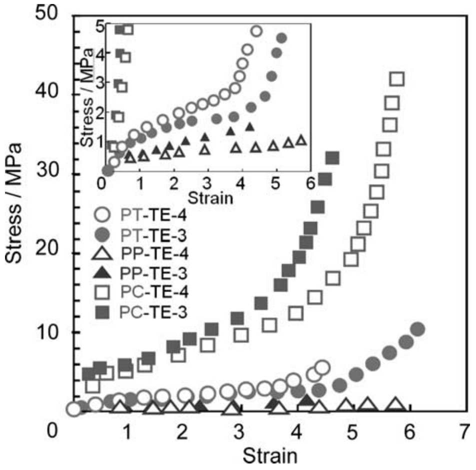

Fig. 8. Stress–strain curves for the PCL-, PPG- and PTMG-based TEGDI–PUEs with $K=3$ and 4 at 25 °C.

and tensile strength than the crystallizable PTMG ones. The Young's modulus and tensile strength of the PPG-based PUEs with $K=3$ were 0.8 and <1 MPa, respectively. The PUEs synthesized with non-crystalline PPG and TEGDI gave a highly softened PUEs.

4. Conclusions

The PUEs were synthesized with PTMG as a polymer glycol and TEGDI or HDI as a diisocyanate. The TEGDI-based PTMG–PUEs showed a weaker phase separation in comparison with the HDI ones. Also, the TEGDI-based PTMG–PUEs have quite larger strain at break and lower Young's modulus than the HDI ones. The highly softened PUEs were successfully obtained by the introduction of the TEGDI as a diisocyanate. Same trends were distinctly observed for the PUEs used PPG and PCL as a polymer glycol. This is attributed to the unique properties of the hard segment, that is, low cohesion force and higher molecular mobility. Since, TEGDI has quite attractive properties, this diisocyanate is expected to another applications such as functional paints, foams and adhesive as well as elastomers.

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