Characterization of the Relaxation Transitions in Toluene Diisocyanate-Based Polyurethanes with Poly(propylene glycol) as the Soft Segment by Thermally Stimulated Current Depolarization with Relaxation Mapping Analysis

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ABSTRACT: Thermal relaxation transitions of toluene diisocyanate (TDI)-based polyurethanes (PU) were characterized by the thermally stimulated current (TSC) technique with verification data from the relaxation mapping analysis (RMA) measurement. TDI-based PU elastomers with poly(propylene glycols) (PPG) as the soft segment and methylene-bis-orthochloroaniline (MOCA) as the hardener, showed three relaxation transitions, (1) a subglass transition (T_g) of the terminal groups occurred near $-135°C$; (2) the T_g; and (3) a global transition occurred above the T_g (assigned as T_{global} transition). The temperature of T_g of PU as expected was varied by the chain length and attributed by the motion of an urethanic chain dominated by the soft segment and may also associate in the cooperative movement with the hard segment. The T_{global} transition appearing above the T_g was identified and attributed to the global transition in the macromolecule scale and was supported by the tangent plot of the dynamic mechanical analyzer (DMA) measurement. The TSC measurement on thermal characteristic transitions of TDI-based PU provided a whole range of thermal transitions including a sub-T_g, the T_g (observed by DSC) to a global transition (may be observed by DMA) with the ease of sample preparation in one single measurement. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 527–545, 1999

Key words: polyurethane; T_g; T_{global}; thermally stimulated current; relaxation mapping analysis

INTRODUCTION

Segmented polyurethanes (PU) based on toluene diisocyanate (TDI) are made by a two-component system, which consists of a TDI–prepolymer and an aromatic hardener such as the methylene-bis-orthochloroaniline (MOCA).[1–7] The prepolymer that contains the soft segment is the essential

part in PU that determines the elasticity. Most often the soft segment used in the preparation of prepolymer is the poly(propylene glycols) (PPG)[5] that constitutes a wide distribution with a repeating unit of $-CH(CH_3)CH_2O-$. This system provides a convenient method for making a variety of PUs from soft elastics to tough and hard materials with the changes, either by the composition or by a structural alternation of the soft segment, such as with poly(tetramethylene oxide),[6,8] poly-caprolactone,[9–12] and/or by the copolymers of polymethylphenylsiloxane[13] and phosphonate[14] or phosphate,[15] among others.[16–19] Consequently, the segmented PU with variations in the widely

distributed soft aliphatic chains and the hard aromatic TDI–MOCA segment in the backbone, often observed with a broadened glass transition (T_g), appeared in the differential scanning calorimeter (DSC) thermogram.[17,20] Thermal analyzers such as the thermal mechanical analyzer (TMA)[21,22] and dynamic mechanical analyzer (DMA)[23–28] are also being used for the measurements of the T_g data. Schneider and Paik Sung used thermal analyzers in their studies of hydrogen bonding in PUs in association with data measured by the infrared spectroscopy,[29,30] and by the small angle X-ray scattering (SAXS).[29,31] They concluded that a high degree of hard–soft segmental mixing occurred in the TDI-based PUs. This mixing phenomenon of the hard–soft segment was also reported by Koberstein Reference problem page 33 (ref 32) in his study with the SAXS in the TDI–ethylene glycol system.[32] One characteristic property of the well-mixed hard–soft segment in PU is its transparent appearance. The other characteristic property is the excellent elasticity[3] often observed in TDI-based PUs. Thermal characteristics[33,34] of the PUs are often expressed by the T_g and measured with thermal analyzers. For example, the difference of the TDI-based to the related segmented PUs of the methylene diphenyl diisocyanate (MDI)–butanediol system[35–37] can be made with the measurement at their T_g by a thermal analyzer such as DSC. The DSC spectrum of the MDI-based PU shows the endothermic peak after the T_g indicating the separated hard and soft domains in the morphology, whereas, the 2,4-TDI-based PU shows only the T_g, indicating the well-mixing of the soft and hard segment. Thermal analyzers of DMA and TMA also provided useful information. The recent innovated thermally stimulated current (TSC) technique provides more sensitive observations on the local and the molecular relaxations of the polymeric materials.[38] Most of the relaxation transitions occurred in the temperature range from −150 to 200°C, including sub-T_g and T_g, could be observed with a simple sample preparation in the TSC measurement. This technique was used in the measuring of T_g of a variety of thermal plastics such as the observation on the multiple relaxation transitions in polystyrenes (PS) that were then attributed to the thermal history for these transitions.[39] The versatility of the TSC depolarization was illustrated in the measurements of T_g of the amorphous thermoplastics, ranging from single-componented macromolecules[40] and copolymers[41] to the blends.[42]

Segmented PU is a copolymer with a long and soft aliphatic segment like a PPG, and a hard segment in combination with the TDI and MOCA aromatic moieties. The localized motions of the segments, or the cooperative motion of the soft segment in association with the molecular backbone, can be measured by the depolarization relaxation technique as long as these transitions occurred in amorphous phase. The study on thermal characteristics of T_g of the PUs is therefore most suitable with TSC technique with the relaxation mapping analysis (RMA) for additional verification on the T_g assignment.

The aim of this investigation was to characterize the thermal relaxation transitions occurred in the T_g region of the TDI-based PUs by the TSC technique and with the thermokinetic data from the RMA for the verification of the T_g. The resulting TSC data may provide much clearer data for the understanding of the nature of transitions when similar data were compared with the DSC and the DMA measurements.

EXPERIMENTAL

Materials

PPG diols of different molecular weights of 400, 700, 1000, and 2000, commonly known as PPG-400, -700, -1000, and -2000 were supplied by Arco Chemical Taiwan Co., Taipei, Taiwan. A commercial TDI (2,4/2,6 in 80/20 ratio) was purchased from First Chemical Taiwan Co., Taipei, Taiwan. MOCA was purchased from Tokyo Kasei Organic Chemicals, Tokyo, Japan. n-Butylamine (Janssen Chimica, Beerse, Belgium) and m-cresol purple (Merck, Darmstadt, Germany) were purchased locally. 2,5-Dihydroxybenzoic acid (DHB) was purchased from Aldrich, Milwaukee, USA. Isophorone diisocyanate (IPDI) and 1,4-butanediol were gifted from Hon Yi Chemical Taiwan Co., Taipei, Taiwan. Dibutyltin dilaurate (T-12) was purchased from Fluka, Buchs, Switzerland.

Sample Preparation

TDI–prepolymer was prepared with the amounts of TDI and PPG as listed in Table I under N_2 atmosphere at 50°C. The NCO content was determined by a back titration method (ASTM D1638-74) using m-cresol purple as the indicator. The reaction mixture was then added with premea-

Table I Compositions of Prepared Polyurethane Elastomers

Specimens	NCO (%)[a]	Composition (wt %)		
		PPG[b]	TDI	MOCA
TDI-based PU				
PU-PPG-400	4.0	56.7	32.0	11.3
PU-PPG-700	4.0	65.1	23.6	11.3
PU-PPG-1000	4.0	69.3	19.4	11.3
PU-PPG-2000	4.0	74.9	13.8	11.3
IPDI-based PU		PPG	IPDI	MOCA
IPDI-PPG-1000/ MOCA	4.0	64.9	23.8	11.3
IPDI-PPG-1000/ 1,4-butanediol/T-12[c]	4.0	70.2	25.7	—

[a] NCO content was determined by a back titration with *n*-butylamine according to ASTM D1638-74.
[b] 0.05 mol was used for all PPG diols.
[c] T-12 is dibutyltin dilaurate and the content of 1,4-butanediol was 4.1 wt %.

sured MOCA. The well-mixed solution was transferred to a teflon plate and cured for 1 h at 105°C.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer (HP G2025A) used was equipped with a 337-nm nitrogen laser, with 3-ns pulse width duration, and an electron multiplier detector. The instrument was operated in positive ion reflection mode with an accelerating potential of +28 kV. The mass scale was calibrated with peptide standard. DHB was used as the matrix. The data were acquired in an average of 150 laser shots. Aqueous NaCl and KCl solution were added for mass peak identifications.

Differential Scanning Calorimetry

A Du Pont 9000 DSC instrument was used for T_g measurement. Samples were measured at a scanning speed of 10°C/min with the temperature range of −120–200°C. The sample size was ∼ 5–10 mg.

Thermally Stimulated Current and Relaxation Mapping Analysis

A Solomat 9100 (Solomat Co.) instrument was used for the TSC/RMA measurements. The spec-

imens were polarized at 20°C above the T_g with V_p of 100 V/mm. The heating rate of 7°C/min was used for depolarization observation and the sample thickness was about 2 mm. The measured temperature range was −150–100°C.

A 100 V/mm voltage was applied for RMA analysis during the polarization stage. The window width was 5°C. Both polarization and depolarization were 2 min each. The ramping rate during recovery was 7°C/min. The depolarization curves were analyzed with the Debye integration option,[43] and thermokinetic data were provided by the software in the data-collecting microprocessor in the instrument.

Dynamic Mechanical Analysis

DMA was carried out on Polymer Laboratories MK II, with the frequency at 1 Hz and a constant heating rate at 7°C/min. The specimen dimensions were 40 × 8 × 2 mm and the temperature range was from −75 to 100°C.

RESULTS AND DISCUSSION

PU specimens with a difference in the soft chain length were prepared according to the composition listed in Table I. The abbreviations for each specimen in the table are used in this discussion. Scheme I shows the preparation of the TDI-based PUs with the representative structures of prepolymers and the PUs.

PU specimens with 4% NCO content were all transparent. Samples with this low NCO content were intended to minimize the effect of the hard segment.

In Table I, the soft contents are increased from a 56.7% in PU-PPG-400 to a 65.1% in PU-PPG-700, to a 69.3% in PU-PPG-1000, and to a 74.9% in PU-PPG-2000, respectively. Since the molar ratio for all PPG segment remained constant at 0.05 mol, the increased weight percent content is, therefore, only to reflect the increase in the chain lengths. These PPG materials are not available in a single component, so PPG diols were subjected to the analysis by the matrix-assisted laser desorption ionization with time-of-flight (MALDI-TOF) mass spectrometer. Figure 1 shows the individual distribution of the PPG diols. The PPG diols used in this study have a wide distribution.

One of the advantages of measuring the molecular distribution of the samples by MALDI-TOF is that the distribution is presented by the true

Scheme 1   Preparation of TDI-PPG prepolymer and cured with MCCA hardener.

mass and in a readable profile. In addition, the mass and the distribution profile can be further checked by the addition of cationic solutions. One of the simplest methods for the verification is the addition of salt solution to the sample. It requires only the addition of a small amount of salt to the sample solution before carrying out the measurement as usual.

The advantage of the cationic addition to the sample is the observation of the intensified mass peak that contains the cation. With Na and K having masses of 23 and 39, respectively, the mass spectra shifted to a larger mass unit as can be seen in Figure 2. The $M + Na^+$ peaks of each component were intensified as compared to the untreated sample in Figure 2 from (a) to (b), whereas the shift in $M + K^+$ peaks to the higher mass units can also be seen in Figure 2(c). With the observations of the same distribution in both Na^+ and K^+ samples, the distributions may be calculated by the relative abundance in the spectra in this particular case. The results are tabulated in Table II.

With this mass information, the repeating unit, n, in structure shown in Scheme I can be determined. The main components of PPG diols are 424 m/z with $n = 7$ for the PPG-400, 714 m/z with $n = 12$ for PPG-700, 1004 m/z with $n = 17$

for PPG-1000, and 2048 m/z with $n = 35$ for PPG-2000, respectively.

Thermal Evaluations of Polyurethane Elastomers

DSC Measurement

Figure 3 shows the DSC measurements for these PUs. The T_g is increased from the longer chain length of PU-PPG-2000 at $-49°C$ to PU-PPG-1000 at $-26°C$, to PU-PPG-700 at $-14°C$, and to PU-PPG-400 at 20°C, respectively.

With a constant molar ratio of the soft segment in PU specimens, the increasing T_g in Figure 3 is related to the variation of the chain length. As expected, the shorter the chain length, the higher the T_g. The change in T_g may be attributed to the stiffness of the chain length, as it was increased from the main component at $n = 35$ for PU-P-2000 to PU-P-400 with the main component at $n = 7$.

TSC Measurement

The global TSC spectra of PU-PPG-400, -700, -1000, and -2000 are shown in Figure 4. Each spectrum consists of four distinguishable peaks. These peaks are designated as α, β, γ, and δ peaks

Figure 1   MALDI-TOF spectra of PPG diols (a) PPG-400, (b) PPG-700, (c) PPG-1000, and (d) PPG-2000.

Figure 2 MALDI-TOF spectra of PPG-1000 diol (a) reference, (b) sample with Na^+-salt addition, and (c) sample with K^+-salt addition.

in decreasing order of the temperature. In addition, α_1 and β_1 peaks are assigned for the PU-PPG-400, α_2 and β_2 peaks for the PU-PPG-700, α_3 and β_3 peaks for the PU-PPG-1000, and α_4 and β_4 peaks for the PU-PPG-2000, respectively. To simplify this discussion, these γ and δ peaks shown in the inserted diagram in Figure 4 are not individually labeled, since these two peaks are not greatly affected by the chain length.

These four peaks need to be clarified. To test the nature or origin of the TSC peaks, two recommended[44] methods were used.

The first method is the test of the reproducibility. The performance by repeating runs may provide the evidence of the consistency and/or reproducibility of the spectrum. At the same time, it may eliminate peaks or transitions resulted from the thermal history. Figure 5 shows the consistency of the peaks for α, β, and δ transitions but not for the γ peak, which diminishes with consecutive runs. The diminishing γ peak can also be seen with the annealed samples in Figure 6. This diminishing γ peak with an increasing and a slightly decreasing in β peak [Fig. 5(a)] were noted from these experiments and may be attributed to the increases in the structural orderliness. A slight increase in δ peak was observed in the inserted diagram in Figure 5(b). This slight increase in δ peak is insignificant, since the change in observation is at a low intensity of 10^{-14} A.

The diminishing values in the γ peak as observed in Figures 5 and 6 may indicate the temporary nature of this peak, probably reflected by the insufficient mixing in the hot-melt preparation among other possibilities.[45] A noticeable in-

crease in α peak accompanying each diminishing of this interfacial peak is observed in these repeating runs. Apparently, this γ peak represents the relaxation of the inhomogeneous or constrained amorphous phase that was then converted to the homogeneous amorphous phase after the heating treatment.

Table II Distribution[a] of the PPG Soft Chain

n (repeat unit)	PPG-400	PPG-700	PPG-1000	PPG-2000
5	3.5			
6	14.4			
7	28.9			
8	27.9	3.1		
9	15.4	6.8		
10	5.5	13.7		
11	3.0	16.4	1.9	
12	1.4	16.8	3.9	
13		16.4	5.8	
14		12.0	9.7	
15		7.2	10.0	
16		4.5	11.4	
17		2.1	12.3	
18		1.0	10.4	
19			9.7	
20			9.2	
21			5.8	
22			4.1	
23			2.4	
24			2.2	1.1
25			1.2	1.3
26				2.4
27				2.7
28				3.9
29				5.2
30				5.2
31				6.9
32				7.1
33				7.4
34				8.2
35				7.4
36				7.6
37				7.1
38				5.8
39				4.9
40				4.5
41				3.4
42				2.5
43				2.4
44				1.6
45				0.8
46				0.6

[a] Distribution percents were calculated by relative abundance of MALDI-TOF spectra.

Figure 3 DSC spectra of PU elastomers (a) PU-PPG-400, (b) PU-PPG-700, (c) PU-PPG-1000, and (d) PU-PPG-2000.

The second test that was carried out for the differentiation of the real transition such as T_g from the free space discharged peak, such as the $T_{g,\rho}$.[39,41–43] For the α peak appearing at the highest temperature region in the TSC spectrum, it may or may not be the real transition. For the real transition, such as the T_g, it was expected to observe the overlapping peaks[46] occurring with the variation of the polarization voltages (V_p). Figure 7(a) shows the overlapped peaks for both α

and β, indicating that these two peaks both represent the real transitions. The linear correlation[44,46] of the current/intensity with variation in V_p as shown in Figure 7(b) confirms that the two real transitions occur at this region.

Furthermore, samples from different chain lengths of PPG segment, (i.e., PU-PPG-400, -700, -1000, and -2000) are all presented with a similar pattern in TSC measurements. The observations of these two peaks (α and β) as the real transitions, indicate that the TSC instrument is capable of observing the relaxation transitions adjacent to each other in the amorphous region/phases of the TDI-based PU elastomers. Similar observation of two peaks at a high temperature region for the segmented PU based on MDI specimens was reported[47] with a much weaker intensity and was attributed to the observation of the localized and interfacial relaxation in the MDI-based PUs. The assignments on these depolarization transitions are as follows.

The Assignment of the δ Peak. PUs and other thermosetting plastics often show the relaxation transitions of terminal and free groups at -140 to $-130°C$ region.[48,49] The δ peak at $-135°C$, is therefore assigned as the relaxation of the free and terminal groups of TDI-based PU with PPG

Figure 4 TSC spectra of PU elastomers (a) PU-PPG-400 (line a), (b) PU-PPG-700 (line b), (c) PU-PPG-1000 (line c), and (d) PU-PPG-2000 (line d).

Figure 5   TSC spectra of TDI-based polyurethane elastomers of PU-PPG-1000 subjected to six consecutive runs (a) global spectra and (b) expansion spectra at the lower temperature range.

Figure 6   TSC spectra of PU-PPG-1000 (a) before and (b) after annealing at 120°C for 30 min.

soft segment. This relaxation is not affected by the change of chain length (Fig. 4) or subjected to the repeating runs (Fig. 5) and the heat treatment (Fig. 6). Apparently, this relaxation transition requires little energy for the free and terminal groups to be polarized. Consequently, the relaxation transition is not affected by the change of the polarization voltages nor the change of the specimen's chain lengths.

The Diminishing of the γ Peak. The diminishing of this sub-T_g relaxation peak (i.e., γ peak), in TSC spectrum is not unusual. Often this type of peak appears in the region of -110 to $-90°C$ region.[49] There are many possible sources for this peak. It was seen with a specimen that was not completely mixed and is often observed in specimens prepared from the hot-melt method. It is also associated with the relaxation of the aromatic segment such as bis-*p*-phenol A (BPA) in diglycidyl ether of bisphenol A (DGEBA) resins.[49] It was also observed in TDI-based PU specimens with soft segments of poly(tetramethylene oxide) (PTMO) and polycaprolactone (PCL) in a related study.[8,9] It could be attributed to the interfacial relaxation transition, since the diminishing of this peak corresponded to the increasing intensity in α peak as seen in Figures 5 and 6. With the

thermal annealing process, specimens generally release the area constrained to a more uniformed phase. For TDI PU specimens, the disappearance of this γ peak may or may not be associated with the formation of hydrogen bonding of the hard segment to the soft segment, as TSC is not equipped to observe the relaxation of the rigid or crystalline domain. For the same reason, the TSC observation on the relaxation peaks must be located in an amorphous region.

The β Transition. The source for this β relaxation transition is associated with the molecular motion dominated by the soft segment. This is especially true for the testing specimen (i.e., PU-PPG-1000 consists of approximately 70 wt % of the soft segment). This peak is regarded as the T_g for the specimen. This assignment is assured with the observation on the shifting of the β peak to a lower temperature from 30 to $-46°C$ as the PPG segment increases from $n = 7$ to 35 in the chain lengths (line a to d in Fig. 4). It is common to observe the lowering of T_g with the longer soft chain through the easier cooperative motion of the matrix of the PUs as the T_g is observed at 30°C for PU-PPG-400, 0°C for PU-PPG-700, $-24°C$ for PU-PPG-1000, and $-46°C$ for PU-PPG-2000, respectively, in these measurements.

Figure 7 TSC spectra of α and β peaks of PU-PPG-1000 via varied voltage applied with 10, 30, 50, 70, 90, 110, 130, 150, 170 and 190 V/mm. (b) The dependence of applied voltage versus current/intensity for α and β peaks PU-PPG-1000.

The α Transition. As previously mentioned in the peak assignments, this α transition is a real transition. Then what is the nature of this α transition?

An argument on this highly intensified peak could appear as the $T_{g,\rho}$,[39] as it is often observed at the higher temperature just above the T_g for polymers. However, along with evidence from the testings with repeating runs (Fig. 5), the annealing process (Fig. 6), the observation of the overlapped peaks in Figure 7(a), the linear correlation in current/intensity with variation in the polarization voltage (V_p) in Figure 7(b), and supported

with similar observations in the various soft segments in PTMO[8] and PCL,[9] the assignment of $T_{g,\rho}$ for this α peak can be ruled out.

Implications of these two peaks of α and β as the real transitions such as the T_g indicate that PU elastomers of TDI-PPG/MOCA system might possess the dual T_g. However, as the specimen consists of 70 wt % of the soft segment, and this main chain is set in motion and observed as the T_g relaxation at β transition, it is not realistic to observe the additional T_g generated by the remaining 30 wt % of the well-mixed hard segment in the amorphous phase. It is unlikely that the

Figure 8 TSC spectra of PU-PPG-1000 (a) using with TDI cured with MOCA, (b) using with IPDI cured MOCA, and (c) using with IPDI cured 1,4-butanediol-dibutyltin dilaurate.

hard segment can manage to give a T_g of its own at a higher temperature, especially as the hard segment is situated within the soft segment and does not exist in the separate domain. Furthermore, no known evidence of the dual T_g for 2,4-TDI-based PU was observed by DSC or SAXS among other instruments cited in the literature.[21,29,30]

All our PU specimens are in clear transparency. Furthermore, this α transition was observed with a high intensity in TSC spectrum, indicating that the electrets responsible for this α transition are both rich in polarity and in a highly mobile state in amorphous state and not in the separated domain or in semicrystalline form.[50] Without the separated domain, it is hard to rationalize the hard segment of TDI or TDI–MOCA segment that can provide the T_g of its own. TDI–MOCA segment in our system existed in the well-mixed amorphous phase as no endothermic peak up to 200°C for PU-PPG-1000 was detected in the DSC measurement. Therefore, the hypothesis of a dual T_g for TDI-based PU was ruled out.

Therefore, this α transition observed in TDI-based system may result from the global transition, which consists of the entire environment of the well-mixed hard segment dispersed in the amorphous soft segment. The aromatic ring of the TDI as the electret possesses a rather rich polarity, and with free mobility in the amorphous phase, it can be polarized with ease. Upon the depolarization process, the aromatic TDI electrets release the high current/intensity as observed in

TSC spectrum in Figure 4. This α transition may be attributed to the global motion of the macromolecule scale as the TDI moiety is widely spread in the amorphous phase. To check the electronic nature of the TDI as the electret, two samples based on the aliphatic IPDI were prepared (Table I) and designated as IPDI-PPG-1000/MOCA and IPDI-PPG-1000/1,4-butanediol/dibutyltin dilaurate (T-12) specimens. Figure 8 displays TSC spectra for these two specimens with the TDI-based sample as the reference. The intensities/current of these IPDI-based samples in TSC spectra are much weaker compared to TDI-based sample, so this weaker intensity of the α transition may be attributed to the aliphatic and nonpolar nature of the IPDI segment. Therefore, the high current/intensity generated from the depolarization relaxation transition may be attributed to the TDI aromatic moieties as the electrets in amorphous state. However, polarity of the electrets alone is not the sole source of the high intensity in the TSC spectrum. Pissis and associates showed a weaker intensity of a transition at this region of the MDI-PTMO-based PU,[47] indicating that the rigidity of the highly polarized aromatic MDI as the electrets may only give a weak signal. So the mobility of the TDI moiety as the electret, which is situated in the amorphous phase in the well-mixed fashion with the soft segment, may provide both polar nature needed as the electrets and the free motion for the high intensity observed in the TSC spectrum (Fig. 4). By doing so, the high intensity of PU-PPG-1000

(a): DSC vs. DMA

(b): TSC

Figure 9   Comparative thermal data from DSC, DMA, and TSC on PU-PPG-1000 (a) DSC versus DMA and (b) TSC.

specimen in TSC spectrum may imply that the depolarization signal results from the global movement of the PU. Also, this global movement may be in the macromolecular scale, since this transition takes place after the T_g.

To test this assumption, PU-PPG samples were prepared and subjected to the DMA analysis. DMA is known to provide the thermal mechanical properties, and thus may reflect the macromolecular nature of the polymeric materials. The DMA measurement in terms of tan δ curve on the PU specimens was conducted and plotted in Figure 9 with the DSC in (a) and with TSC as the reference in (b). The results depict that the β transition (the T_g) in TSC is in agreement with the T_g in DSC and the α transition agrees with the tan δ_{max} value in the tangent plot of the DMA. The com-

parative data confirm that the nature of the α transition is related to the global transition. Therefore, this α transition is reassigned as the T_{global} transition for the TDI-based PU elastomers.

RMA Measurement

The RMA measurement was carried out according to the general procedure. The polarization on the specimen was applied according to the TSC measurement. However, an additional step was added before cooling the specimen. The specimen at a set temperature was polarized and then the temperature was lowered to the preset temperature. At this point, the voltage was removed and the specimen was quickly quenched to −40°C be-

Figure 10 RMA spectra of PU-PPG-700 (a) elementary peaks recorded with a 5°C window, (b) Arrhenius-Eyring, and (c) the compensation search.

low the polarization temperature. The RMA operational procedure was then carried out, similar to that of the TSC measurement.

One of the advantages of the thermal windowing technique is the dynamic evaluation of the relaxation transition in much detail, enabling the

confirmation of T_g observed in global TSC spectrum. The relaxation transitions, especially the β (T_g) and the α (T_{global}) transitions in the PU specimens, need to be studied and to characterize the nature or the source of each transition.

The thermal windowing technique provides the observation of a narrowed peak in the global spectrum obtained by the TSC. Each peak observed at a given polarization temperature can be fitted to an Arrhenius eq. (1), as it was provided in the software,[43]

$$\tau_i(T) = \tau_{oi}exp(\Delta H/kT) \tag{1}$$

where τ_{oi} is the pre-exponential factor, ΔH and k are the activation enthalpy and Boltzmann's constant, respectively.

As indicated by Ibar,[51] the pre-exponential factor in the Arrhenius equthar is directly related to the entropy of activation.

For a given relaxation mode that is isolated by polarizing at T_p, the relaxation time can be expressed as:

$$\log \tau_i = \log(\tau_{oi})+\Delta G/kT \tag{2}$$

$$\Delta G = \Delta H_p - T\Delta S_p \tag{3}$$

where the subscript p indicates that these variables are function of the polarization temperature. The Eyring equation[51] is given in eq. (4),

$$\log(\tau_{oi}) = -\log(kT/h) \tag{4}$$

where k and h are the Boltzmann and Planck's constants, respectively.

The overall equation in logarithm form [eq. (5)] is used in the software for the calculations of ΔH_p and ΔS_p,

$$\log \tau_I + \log T + \log(k/h) = -S_p/k + \Delta H_p/kT \tag{5}$$

A plot of $[\log \tau_i + \log T + \log(k/h)]$ versus polarization temperature (T_p) gives the slope $(\Delta H_p/k)$ and intercept $(-\Delta S_p/k)$. The Arrhenius or Eyring lines may converge to a single point (i.e., the compensation point, T_c). The coordinates $[T_c, \log \tau_c]$ of the T_c is important because it may transcribe the cooperative characteristics of different relaxation as Arrhenius lines converge to a single point.[52]

The RMA measurement was carried out for these PU elastomers. Figure 10 shows the RMA

Figure 11 The Entropy–Enthalpy (E–E) plot of PU-PPG-700.

spectra of PU-PPG-700, (a) elementary peak recorded with a 5°C window, (b) the corresponding Arrhenius–Eyring plots in which non-Arrhenius lines/curves are observed as to separate the Arrhenius lines into two sections, and (c) the T_c from Arrhenius lines for β (T_g) transition.

Another set of straight lines appeared in α (T_{global}) transition region, but does not converge to form a compensation point. These nonlinear lines/curves that separate the T_g and T_{global} represent the interfacial transition. The T_g and T_{global} that coexisted in an adjacent region in the amorphous phase of PU elastomers are therefore confirmed.

Thermal windowing technique in RMA measurement provides a convenient method for the verification of T_g. For a T_g, it is required that each of the thermal windowing curves from the β-peak range gave a straight line (Arrhenius line) that all converged to the compensation point, T_c. The T_g data for these PU elastomers are in agreement with the general observation of $T_c > T_g$ for polymeric materials.[43,38] The compensation search also provided a series of thermokinetic data listed in the Eyring table from the printout. The $(T_c, \log \tau_c)$ of T_c for this β transition (T_g) is $(35.7, -2.75)$ and is seen in Figure 10 for the PU-PPG-1000 specimen.

The verification work on the T_g can also use the thermokinetic data of ΔH_g and ΔS_g [i.e., the intercept of the positive and negative compensation lines in the Entropy and Enthalpy (E–E) plot as shown in Fig. 11]. This gave the maximum values for ΔH_g and ΔS_g at the T_g. The related data are listed in Table III and the calculated T_g values from RMA are in agreement with the T_g measured by the TSC. The chain length effect on the ΔH_g and ΔS_g can also be seen from Table III. ΔH_g

Table III Verification of the T_g Temperature of the TDI-Based PU Elastomer by the Compensation Search in RMA Measurement

Specimens	TSC[a] β	RMA[b]				DSC[c]
		Method 1	Method 2			
			ΔH_g (Kcal/mol)	ΔS_g (cal/K)	T_g (°C)	
PU-PPG-400	30	34.4	58.2	119	29.8	20
PU-PPG-700	0	2.3	51.6	121	0.5	−14
PU-PPG-1000	−24	−21.1	47.2	121	−23.3	−26
PU-PPG-2000	−46	−45.5	44.5	132	−45.2	−49

[a] Measured with V_p = 100 V/mm, with depolarization 7°C/min from −150 to 100°C.
[b] RMA measured by thermal windowing technique with V_p = 100 V/mm, with width of 5°C. Method 1: Based on Eyring table provided from the software in Solomat 9100. Method 2: Based on maximum data of ΔH_g and ΔS_g on Entropy–Enthalpy plot.
[c] Measured at 10°C/min.

(Kcal/mol) decreased from 58.2 with $n = 7$ in PU-PPG-400 to 44.5 with $n = 35$ in PU-PPG-2000, and ΔS_g (cal/mol) increases with the increase in the chain length from 119 in $n = 7$–132 in $n = 35$ in these PU elastomers.

The Dielectric Analyzer Simulation

One of the advantages of running RMA experiments is that the data obtained in RMA can be used to simulate the DEA plot. Figure 12 demonstrates a simulated DEA spectrum of PU-PPG-700. A merging of the two (α and β) peaks can be seen as the frequency increases, whereas the adequate resolution is obtained at the low frequency. The spectrum at low frequency resembles the TSC measurement as shown in Figure 4. TSC spectrum, therefore, may be regarded as the DEA measurement in the low frequency but with much

Figure 12 The 3D graphic spectra as dielectric loss constant E″ versus temperature and frequency for PU-P-700.

Figure 13 DMA spectra of polyurethane elastomers (a) storage modulus (E') and (b) tan δ; symbols of square, circle, up triangle, and down triangle represent PU-PPG-400, PU-PPG-700, PU-PPG-1000, and PU-PPG-2000, respectively.

simpler sample preparation and accurate measuring of the T_g.[50]

DMA Measurements

To gather the additional information of the global/mechanical thermal transition that may be related to the general appearance and authenticity of the T_{global} transition in the TSC spectrum, some DMA specimens of TDI-based PUs corresponding to these specimens measured by TSC technique were prepared and subjected to the DMA measurement. The additional specimens used were PU-PPG-400, -700, and -2000 with PU-PPG-1000 as reference. The measurement was carried out at a frequency of 1 Hz, a constant heating rate of

7°C/min, and the specimen thickness of 2 mm. Figure 13 contains the DMA data, where the temperature plot with the storage modulus (E') is shown in (a) and the tan δ plot in (b). The energy requirement for the storage measurement was in association with the chain length and in response to the stiffness of the specimens. The energy decreases as the chain length increases. E' of 9.25 Pa was found for the chain length of $n = 7$ (main component) in PU-PPG-400, whereas the E' was decreased to 8.8 Pa for the $n = 35$ in PU-PPG-2000 specimen. The gradual ease of the E' curves from PU-PPG- series of -400 (solid square), to -700 (open circle), to -1000 (solid triangle), and to -2000 (open triangle) can be seen as the slopes are lowered as the stiffness of the

(a): DSC vs. DMA

(b): TSC

Figure 14 Comparative thermal data from DSC, DMA, and TSC on PU-PPG-Specimens (a) DSC versus DMA and (b) TSC; 1, 2, and 3 represent PU-PPG-400, PU-PPG-700, and PU-PPG-2000, respectively.

specimens decreases in Figure 13(a). The corresponding temperature of the maximum peaks in tan δ curves (tan δ_{max}) for PU specimens varied with the chain lengths and lowered from 44°C for n = 7, to 21°C for n = 12, to 2°C for n = 17, and to -14°C for n = 35 in Figure 13(b). These tan δ_{max} data represent the mechanical responses of the specimens. These tan δ_{max} appeared in the similar temperature region as the T_{global} transition measured by the TSC technique. A combined spectra on the thermal transitions of T_g in DSC and tan δ_{max} curves from DMA are shown in Figure 14(a) and the β (T_g) transition and the α (T_{global}) transition from TSC are shown in Figure 14(b). These additional PU specimens possess the similar patterns of β (T_g)

and α (T_{global}) transitions to that of the PU-PPG-1000 specimen shown in Figure 9, indicating that the generality and the authenticity of the T_{global} transition appears above the T_g for the TDI-based PU elastomers. The T_{global} transition from TSC in the general region appears similar to the tan δ_{max} peak from the DMA. This T_{global} transition seems to possess similar, yet with some different global properties, measured by both the TSC and the DMA. The T_{global} transition in TSC, as it was indicated, may relate to the domination of the hard segment of TDI moieties as the electrets in amorphous phase, while the tan δ_{max} value may indicate the hard segment domination in the global properties as measured in the storage modulus with

the association with the loss modulus for the tan δ_{max} value. The difference of T_{global} transition in TSC and the tan δ_{max} values may attribute also to the sample preparation, as well as to the different global and mechanical responses measured by these two different thermal analyzers. Further investigations on T_{global} transition with the different contents of TDI hard segments are in progress.

CONCLUSIONS

Thermal relaxation transitions in the segmented PUs were examined by TSC technique. A T_g and a T_{global} were found in the T_g region. The depolarization relaxation that occurred in the T_g is dominated by the urethanic chain motion. The T_{global} is attributed to the global motion consisting of the hard–soft segment well mixed in an amorphous region. The T_g is influenced by the soft segment, which is in cooperative motion with the hard segment. The PPG chain length shifts the T_g to a lower temperature with longer chain length. The T_{global} transition that occurred above the T_g is the global motion in macromolecular scale dominated by TDI-MOCA aromatic segment. However, it is sensitive to the thermal history in the sample preparation. The observation of T_{global} was supported by the DMA measurement as indicated by the tan δ_{max}. TSC measurement provides a whole range of thermal transitions that includes sub-T_g of the localized relaxation, in addition to the T_g and the T_{global} that was supported by the DMA observation. TSC measurement provides an easy sample preparation and accurate data in a single measurement.

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