



Thermal analysis of polyurethane elastomers matrix with different chain extender contents for thermal conductive application

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Abstract

Polyurethane elastomers (PUR) based on polypropylene glycol and 4,4'-diphenylmethane diisocyanate were prepared with various monoethylene glycol (mEG) contents. The aim of this study is to find a reliable polymer matrix for composites of improved thermal conductivity and testing fully in order to collect knowledge about its structure. Thermal conductivity was improved from 0.255 to 0.329 W m⁻¹ K⁻¹ when increasing chain extender content. This attributed to a high appearance crystalline ordering level when adding high mEG content. Differential scanning calorimetry revealed a low transition temperature of soft segment at the same temperature around - 64 °C, due to constant polyol content. The enthalpy of melting increases with increasing mEG content. This is due to the increasing crystalline phase and hard segment phase separation within the PUR structure. Dynamic mechanical analysis results show the glass transition temperature of soft segment in the same temperature range between - 57 and - 52 °C and intensity peak of tanδ tends to decrease when mEG content was increased. On the other hand, the glass transition temperature of hard segment tends to increase from 10 to 93 °C and has high intensity peak of tanδ with increasing mEG content. Increasing the chain extender content can be enhancing the hard segment length in PUR structure and affecting both soft segment motion and hard segment motion. Increasing hard segment length might be obstructing soft segment motion and influence hard segment motion which is hard to move at low temperatures. Phase separation of soft and hard segment clearly observed using the DMA technique.

Keywords Polyurethane elastomers · Chain extender · Structural polymer · Thermal analysis

Introduction

Polyurethanes are widely used in industry and have wide range of applications. Polyurethanes have several advantages consisting of high impact strength, good elasticity, high elongation, abrasion resistance, excellent resistance to oils and solvents, good tear resistance and so on [1]. However, polyurethanes have low thermal conductivity, hence many efforts trying to improve their properties and especially thermal conductivity. Polyurethanes are organic polymers that contain the urethane groups in their structure. They are typically made by the reaction of a polyol with a

diisocyanate. It contains two separate structural phases consisting of a hard segment and a soft segment. Polyol structure is related to the reaction of diisocyanate with hydroxyl groups of chain extender and polyol. Elastomeric behavior of polymeric systems can be attributed to microphase separation of the hard and soft segments. The rigid domains reinforce the elastomeric matrix like covalent linkages in cross-linked elastomers. Consequently, the effective parameters on the properties of PUR are soft segmental chemical construction, hard segmental chemical construction and relative size between the soft and hard segments. The chemical constructions of segments are related to the type of polyols, diisocyanate and chain extenders used in the composition. Furthermore, the last factor changes with the choice of different molar ratios of raw materials [2]. Thermal conductivity can be determined by the structure of the polymer as well as the morphology of the polymer. There is a large scatter in the reported experimental data of thermal conductivity of crystalline

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polymers. It should be noticed that the thermal conductivities of polymers depend on many factors such as chemical constituents, bond strength, structure type, side group molecular weight, molecular density distribution, type and strength of defects or structural faults, size of intermediate range order, processing conditions and temperature [3].

Chain extenders are reactive low molecular weight compounds such as hydroxyl amines, glycols and other types, and diamines are used to influence the end properties of polyurethanes during their synthesis [4]. Two main groups are used as chain extenders such as aromatic diols or diamines and the corresponding aliphatic diols or diamines. The choice of a chain extender depends on the properties required and the process conditions. Chain extender may increase the hard segment length to allow hard segment segregation which results in good mechanical properties such as an increase in modulus and the hard segment glass transition temperature of polyurethane [5–14]. In general, PUR chain extended with an aliphatic diol to produce a softer material than do their aromatic chain extended counterparts. Also, diamine chain extenders are much more reactive than diol chain extenders and give properties superior to those of similar polymers prepared with the equivalent diol chain extenders. This is due to the hard segment (urea linkage) which has a higher density of hydrogen bonding, resulting in a higher glass transition temperature and higher thermal stability. Moreover, due to electron delocalization in the aromatic chain extenders, they have less reactivity than aliphatic chain extenders which can be favorable in reactions that need to be highly controlled [15]. There were several works explaining about the effect of chain extenders in PUR properties. For example, effect of chain extender on mechanical properties of PUR was investigated. Tensile strength was increased by the ethylene glycol but had negative influenced on the elongation at break [16]. Ethylene glycol was used as chain extender in polyurethanes synthesis. The formula has affected the polyurethane's properties, like density, impact resilience, compression set, water absorbency behavior and cellular morphology a great deal in comparison. Results show these properties are dependent on the chain extender content in the polyurethane compound [17]. Butanediol shows properties superior to other extenders. The superior performance of butanediol as an extender can be explained on the basis of structural regularity formed by the acid component in the polyester [18]. Chain extender type and urethane group content on the mechanical properties was studied. The best mechanical behavior as elastomers was achieved for polyurethanes with even numbers of CH_2 on the chain extender, so the different parts of PUR macromolecular chains can adopt extended linear forms [4]. Elastomers with larger chain extender molecular have

larger hard segments and better phase separation. The ratio of the hard to soft segment content has effects on phase separation, good physical and mechanical properties [2, 4]. The effect of the incorporation of various new chain extenders on mechanical and thermal properties of PUR was examined. Longer chain lengths between cross-links produce higher elongations at break and lower modulus. The branched chains of the difunctional chain extenders decrease the physical cross-link density and thus decrease in the mechanical strength. The cross-linking process increases the urethane domain's rigidity and decreases the soft segment's crystallinity. These factors enhance the tensile strength of the materials [15]. The glass transition temperature of materials increases with increasing hard segment content. Interchain cross-linking improves thermal stability. The structure and amount of hard segments cause a significant variation in the properties of cross-linked elastomers [19]. Effect of the chemical nature of chain extender on both phase separation and final properties of the polyurethane dispersions was also examined. Diols are used as chain extenders. A higher degree of crystallinity in the polyurethane structure is obtained due to the increased phase separation because of increasing the chain extender length which produces an increase in the adhesion values when molecular weight of the chain extender is increased [11]. A systematic investigation is made on the effect of the chemical structure of chain extenders on the physical and thermal properties of polyurethanes [20]. Spectroscopic, mechanical and thermal data reveal that polymer properties can be significantly altered by differences in chemical bonding within the chain extender's backbone. Although all data support the expected differences in phase morphology between the two series of samples, they also suggest that increasing the chain extender's unsaturation reduced its reactivity with isocyanate, also adversely affected hydrogen bonding, lowered the degree of crystallinity of the hard segments and decreased phase separation [21]. Thermal and mechanical properties are discussed from the viewpoint of microphase domain separation of hard and soft segments. It resulted in negative deviation in the modulus of the polymers. It may be due to the bulky structure and strong cohesive force of the urea groups [22].

From previous studies about the effect of chain extender, thermal conductivity and structural PUR with varying chain extender content were investigated in order to flexible and rigid PUR application by thermal conductivity test, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) method.

Experimental

Materials

PUR were synthesized using polypropylene glycol (PPG-4000) for polyol which reacted with ethylene oxide (ALCUPOL D4011). 4,4'-Diphenylmethane diisocyanate (MDI) was used for isocyanate. Trade name of MDI is ONGRONAT XP 1147. It is an acidified MDI blend based on ONGRONAT 2100, MI50 and pure MDI. Average molecular weight is 266 g mol^{-1} , and equivalent weight is $127.33 \text{ g mol}^{-1}$. In this study, monoethylene glycol (mEG) is used for chain extender. It is produced from ethylene by the intermediate ethylene oxide. Ethylene oxide reacts with water to produce ethylene glycol. DABCO 33-LV is a catalyst in this study, mixture of 33% triethylene diamine and 67% dipropylene glycol. The air release additive is BYK A500, silicone-free air release additive. Furthermore, two types of moisture scavenger are used that consist of Finmasorb 430 PR and Incozol LV. Finmasorb 430 PR is a molecular sieve pasted in castor oil at 50%, and Incozol LV also acts as a moisture scavenger preventing the generation of CO_2 gas. All of ingredients are listed in Table 1.

Methods

Polyol blends were prepared by solution sheared mix with different chain extender contents from 7 to 34 g. Moreover, amine catalyst, air release additive and two moisture scavengers were also solution mixed with the polyol. Then, polyol blend was mixed with MDI part by mass fraction as shown in Table 1. The polyol blend was homogenized using homogenization machine and pre-dried. After that, an acidified MDI blend was added in the polyol blend and shear mixed for 20–25 s at around 1000 rpm and poured into the warm mold of $50 \text{ }^\circ\text{C}$ at least 30 min to form a homogeneous PUR sheet of 1–4 mm thickness. The cured sample sheets were stored for at least 3 days at room temperature before testing. Structural PUR were characterized by DSC technique. DSC of PUR was performed on

METTER TOLEDO model DSC823e with heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ from -100 to $250 \text{ }^\circ\text{C}$. Sample mass of around 10 mg was used, accurately shown in Fig. 3. Dynamic Mechanical Thermal Analyzer MkIII (Rheometric Scientific) was used for DMA tests from -80 to $150 \text{ }^\circ\text{C}$ with heating rate of $2 \text{ }^\circ\text{C min}^{-1}$. The measurement was taken in bending mode at 1 Hz. Thermal conductivity was measured by C-THERM thermal conductivity analyzer (TCi), and the density of PUR was also measured.

Results and discussion

Thermal conductivity and density

Thermal conductivity of PUR with different mEG contents was measured using a TCi Thermal Conductivity Analyzer (C-THERM). Each sample was placed on the sensor and measured at room temperature. A known current is applied to a spiral heating element of the sensor, providing a small amount of heat. This results in a rise in temperature at the interface between sensor and sample which induces a change in the voltage drop of the sensor element. The rate of increase in the sensor voltage is used to determine the thermophysical properties of the sample. The thermophysical properties are inversely proportional to the rate of increase in the sensor voltage. Result shows the variation of thermal conductivity tends to increase with increasing content of mEG chain extender. The highest thermal conductivity is observed at 34 g mEG of $0.329 \text{ W m}^{-1} \text{ K}^{-1}$. Thermal conductivity enhanced around 29% when compared to 7 g mEG content as shown in Fig. 1 and Table 2. This may be due to increasing the crystallinity level when mEG content was increased by cross-linking. The other reason might be due to polymer crystallinity strongly affecting their thermal conductivity. The hard segment content also influences the physical properties of polyurethanes [16]. Besides, thermal stability of the polymer is connected to their chemical structure, the bond energy between individual atoms comprising the material (energy of dissociation into radicals) [3]. Furthermore, the increase

Table 1 Ingredients of polyurethane elastomers

Description	Trade name	Mass/g
Polypropylene glycol (PPG-4000)	ALCUPOL D4011	100
Monoethylene glycol	mEG	7, 10, 22, 30, 34
Catalyst	Dabco 33-LV	0.15, 0.3
Air release additive	BYK A500	2
Moisture scavenger	Finmasorb 430 PR	5
Moisture scavenger	Incozol LV	2.5
4,4'-Diphenylmethane diisocyanate (MDI)	ONGRONAT XP 1117	24–52 ^a

^aVarying with the other ingredients to keep the content of NCO:OH ratio

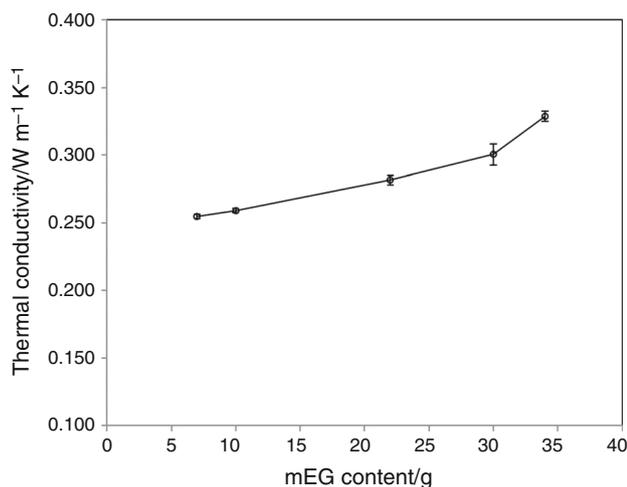


Fig. 1 Thermal conductivity of polyurethane elastomers with various mEG contents from 7 to 34 g

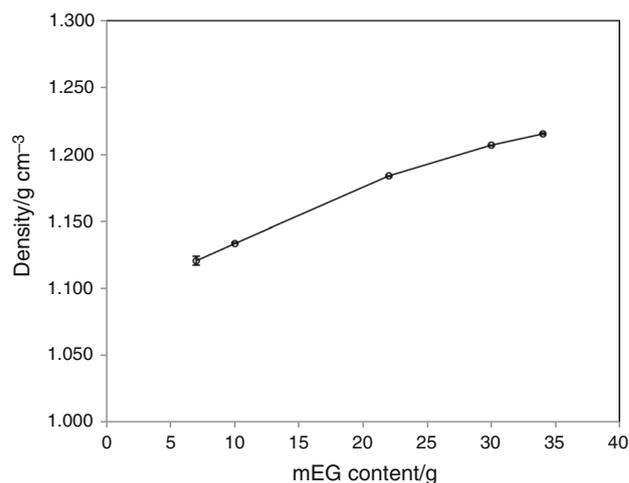


Fig. 2 Density of polyurethane elastomers with various mEG contents from 7 to 34 g

in thermal conductivity related to the increase in density as shown in Fig. 2 and Table 2. Density increases because mEG more easily reacts with MDI and PPG polyol, especially the hard segment in PUR structure and due to the hard segment (urea linkage) which has a higher density of hydrogen bonding [15].

Differential scanning calorimetry (DSC) measurement

To investigate the crystalline phases in PUR microstructure that are formed by the hard segments and soft segments, DSC analysis has been used. DSC curves from the first heating scans of PUR with different mEG contents from 7 to 34 g are shown in Fig. 3. The first heating scans of all the PUR show glass transition of soft segment in the same temperature of about $-64\text{ }^{\circ}\text{C}$ when mEG content was increased as shown in Table 3. However, a relaxation transition could not clearly be observed at high chain extender contents. This may be due to that the cross-linking of the hard segments obscures the PPG polyol segment's motion, which leads to having less soft segments with ordered structures or crystals [15] so they are not clearly registered especially at chain extender contents of 30 and 34 g. The broad endotherms peak at mEG content of 7 g can be suggested to be related to a small degree of ordering

in the hard segment domains. DSC curves reveal a higher degree of the hard segment ordering that exhibited by the presence of endothermic peaks [23, 24]. In case of high mEG contents, endotherm peaks have narrower and higher intensity than the one related to soft segments that may be due to it having higher hard segment contents with more cross-linking than at lower mEG contents.

Figure 4 shows the first derivative of the melting curves of PUR with different mEG contents from flexible to rigid. The first derivative curve of a glass transition gives a peak which area is proportional to the value of ΔC_p . Peak temperature of the first derivative can be used as a measure of change in glass transition temperature. Therefore, the first derivative curves show the glass transition temperature of the soft segments as the same temperature from DSC curve of $-64\text{ }^{\circ}\text{C}$. Furthermore, Table 3 shows enhancement of enthalpy of melting. The enthalpy of melting tends to increase with increasing mEG content. This reveals that the crystalline phase was increased with increasing chain extender content and improved the hard segment phase separation in the PUR structure. Low ΔH_m values at mEG content of 7 g of the endothermic peak indicated the remaining the amorphous structures [25]. Glass transition temperature of hard segment ($T_{g, HS}$) is in the range of $58\text{--}70\text{ }^{\circ}\text{C}$. The chain extender content did not have significant effect on $T_{g, HS}$ on DSC measuring. However, the

Table 2 Thermal conductivity and density of polyurethane elastomers with different mEG contents

mEG content/g	Thermal conductivity/ $\text{W m}^{-1} \text{K}^{-1}$	Density/ g cm^{-3}
7	0.255 ± 0.002	1.120 ± 0.003
10	0.259 ± 0.002	1.134 ± 0.000
22	0.282 ± 0.003	1.184 ± 0.000
30	0.301 ± 0.008	1.207 ± 0.000
34	0.329 ± 0.004	1.215 ± 0.000

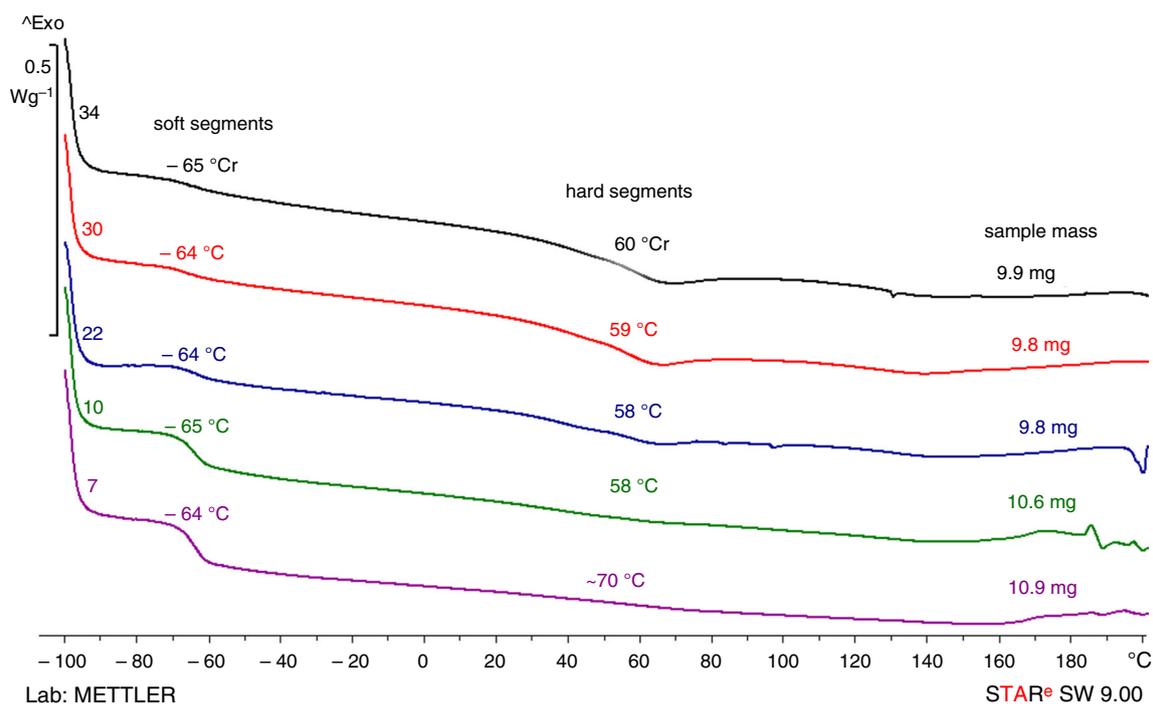


Fig. 3 DSC curves of polyurethane elastomer with various mEG contents from 7 to 34 g

Table 3 Thermal properties of polyurethane elastomers with different mEG contents

mEG content/g	DSC				DMA	
	$T_{g, SS}/^{\circ}\text{C}$	$T_{g, HS}/^{\circ}\text{C}$	$T_{\text{endothermic}}/^{\circ}\text{C}$	$\Delta H_m/\text{J g}^{-1}$	$T_{g, SS}/^{\circ}\text{C}$	$T_{g, HS}/^{\circ}\text{C}$
7	-64	~70	N/A	N/A	-56	10
10	-65	58	62	2.48	-57	28
22	-64	58	64	2.76	-54	73
30	-64	59	65	9.54	-57	84
34	-65	60	67	10.02	-52	93

glass transition temperature of hard segment is difficult which is evaluated by DSC technique because the first derivative shows very small transition.

Dynamic mechanical analysis (DMA) measurement

Dynamic mechanical analysis provides information on viscoelastic properties. The storage modulus (E') provides information regarding the stiffness of the materials, while the loss tangent ($\tan\delta$) measures the degree of molecular motion. The glass transition temperature of the soft segment is defined as the α transition in the $\tan\delta$ curve. Significant features of a $\tan\delta$ plot include the location of the low-temperature maximum where smaller areas are associated with better phase separation of PUR hard and soft phases, as well as less of the hard phase being involved in the glass transition. The magnitude of $\tan\delta$ across the application temperature is proportional to the ratio of

energy absorbed as heat by sample to energy returns as movement of the sample [5].

The storage modulus and $\tan\delta$ of PUR with different chain extender contents are in the temperature range between -70 and 140 °C as shown in Figs. 5 and 6. The E' with various mEG contents is very hard at start temperature, and then, it decreases at low temperatures around -60 °C, and $\tan\delta$ shows a peak associated with the glass transition temperature of the soft segment at the same temperature range between -57 and -52 °C as shown in Table 3. However, intensity of $\tan\delta$ peak of soft segment tends to decrease with increasing mEG content. This is due to low degree of PPG polyol segment motion which relates to DSC curve hard to evaluate a small relaxation of PUR chain at high mEG content. It may be due to the high degree of cross-linking reducing the mobility of the soft segment [26, 27].

In case of high temperature, $\tan\delta$ results exhibit a shift in the curve to higher temperatures and also broadening and

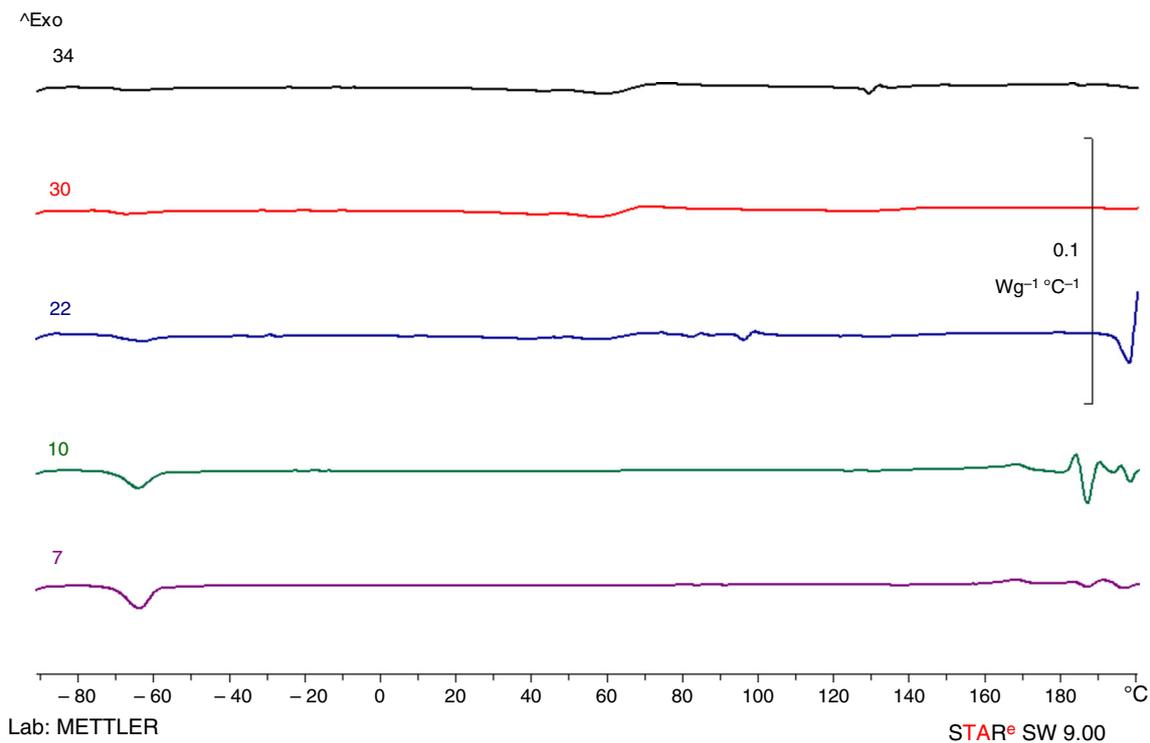


Fig. 4 First derivative from DSC curves of polyurethane elastomer with various mEG contents from 7 to 34 g

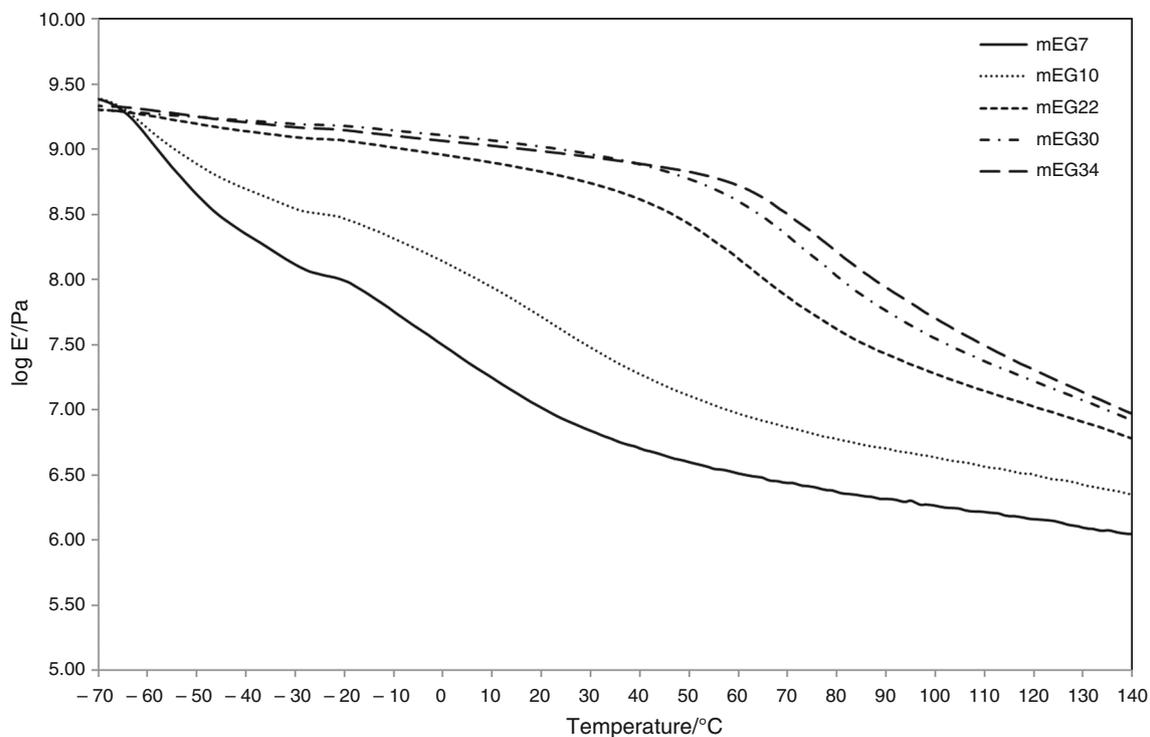


Fig. 5 Storage modulus from DMA of polyurethane elastomers with various mEG contents from 7 to 34 g

high intensity of the peaks with increasing chain extender content as shown in Fig. 6. Table 3 shows the glass transition temperature of hard segment tends to increase with

increasing chain extender content. This increase in melting point is may be due to the increase in the number of higher length hard segment chains in the hard segment domains

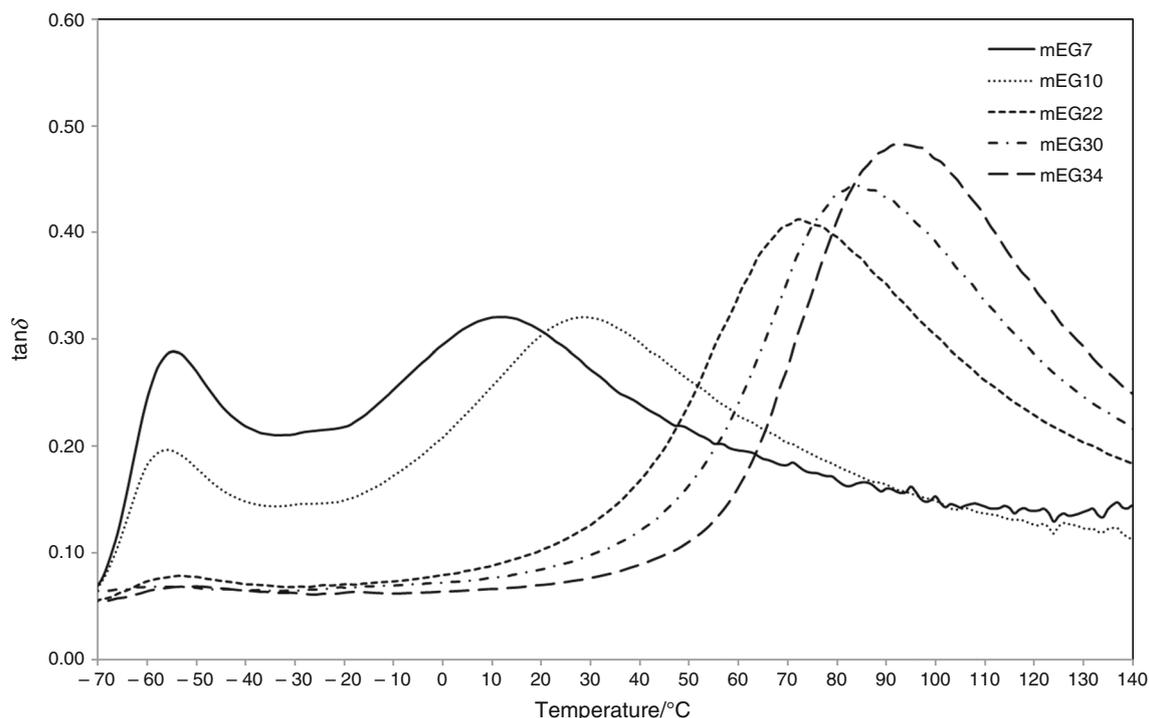


Fig. 6 Mechanical loss factor from DMA of polyurethane elastomers with various mEG contents from 7 to 34 g

that occur as the hard segment content of the polymer is increased [20] and attributed to increasing hard segment crystallinity [28] and phase separation which tend to reduce soft segment mobility. The increasing hard segment resulted in larger hard microcrystalline domains that restricted the molecular motion of the soft segment [5]. Furthermore, the polymer chain with longer chain extender has longer hard segment. The length of hard segment has also effect on phase separation [15].

For flexible PUR at mEG content of 7 and 10 g, E' shows two rubbery regions. The first region at lower temperature from -65 to -29 °C is mainly elastic. After that, E' decreases continually with increasing the temperature. This reveals that the hard segments are not able to form a sufficient amount of physical cross-links. E' of PUR starts to be elastic again at around -10 °C. Anyway, mEG content of 10 g exhibits higher E' value than of 7 g although there is the same pattern. This is due to the high cross-linking of hard segment in PUR structure which affects chain mobility of molecular chain. In case of rigid PUR at high mEG content, storage modulus slightly decreases when temperature was increased at around 40 °C as shown in Fig. 5. Then, it rapidly decreases which can be indicated as melting of the hard segment phases and physical and chemical cross-linking sites between hard segments are totally destroyed [15].

Conclusions

Increasing chain extender content can be increased thermal conductivity of polyurethane elastomers (PUR) because of increasing the crystallinity level by cross-linking in PUR structure. This can be related to a slight increase in density.

Structural phase separation of PUR can be observed from a small relaxation of soft segment hard to evaluate when chain extender content was increased, while the enthalpy of melting tends to increase. These reveal that they gave better hard segment phase although the glass transition of hard segment did not clearly observe in DSC curve.

DMA results both storage modulus and $\tan\delta$ show high hard segment from the cross-linking of chain extender that reacted to isocyanate part in PUR. The glass transition temperature of soft segment did not significantly change, but the intensity of $\tan\delta$ peak tends to decrease with increasing chain extender content. This may be due to a low degree of PPG polyol segment motion. On the other hand, the glass transition temperature of hard segment can be observed and tend to increase when chain extender content was increased. This may be due to increasing the length hard segment chains in the hard segment domains. Flexible PUR show two rubbery regions and lower storage modulus than PUR at high chain extender content. This can also be attributed to high cross-link of hard segment in

PUR structure which affects chain mobility of molecular chain and phase separation.

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