Structure and Physical Properties in Crosslinked Polyurethanes

Véronique Waterlot,[1] Daniel Couturier,[1] Christophe Waterlot[2]

[1]Université des Sciences et Technologies de Lille, Laboratoire d'Ingénierie Moléculaire, Bâtiment C4, 1er étage, 59655 Villeneuve d'Ascq Cedex, France
[2]Groupe ISA, Equipe Sols et Environnement, Laboratoire Génie Civil et géo-Environnement Lille Nord de France (EA 4515), 48 Boulevard Vauban, 59046 Lille Cedex, France

ABSTRACT: Crosslinked polyurethanes based on a mixture of toluene diisocyanate, polypropylene glycol, trimethylol propane (TMP), glycerol (GLY), and desmophen (DES) were synthesized with various ratios of DES and GLY. Chemical crosslinks were introduced through the hard segment (TMP, GLY) and through the soft segment (DES). The effects of the degree of crosslinking on the properties were examined. The crystallinity of the obtained polymers were studied by using modulated differential scanning calorimetry, differential scanning calorimetry, dynamic mechanical analysis and their morphology was studied by atomic force microscopy. It appeared that the degree of crosslinking increased according to the increase of GLY content. Moreover, it was found that chemical crosslinks in the hard segment destroyed the crystallinity of the hard phase and reduced the mobility of the soft phase, improving the heat stability of the hard domains, and modifying the mechanical properties of polyurethane films. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1742–1751, 2011

Key words: polyurethanes; block copolymers; differential scanning calorimetry; atomic force microscopy; mechanical dynamical analysis; tensile testing

INTRODUCTION

Polyurethanes have generated a widespread interest because of their unique combination of unusual properties and their ability to be processed. Segmented polyurethane elastomers are block copolymers comprising alternating sequences of soft- and hard-segments which due to structural and chemical differences, separate into two phases.[1–3] This phase separation occurs because the mainly polar, high melting hard segments are incompatible with the nonpolar, low melting soft segments. Usually, the hard segments have a T_g (glass transition temperature) higher than room temperature while the soft segments are in a rubbery state. Hard domains act as physical crosslinks whereas the soft phase gives extensibility to the polymer. Their biphasic structure explains their excellent mechanical properties. Much work has been done studying the morphology and properties, and their relationship with chemical structure, of the segmented polyurethanes.[4–10]

Polyurethanes are usually obtained from polyglycols and isocyanate to produce isocyanate-terminated polyurethane. Depending on the reactant used to synthesize polymers, properties of polyurethane films such as hardness, stiffness or tensile strength, are influenced by the thermal history of the material and by morphological factors such as degree of hard/soft phase separation, crystallinity, and domain size. Because polyurethane are widely used in many industrial fields such as fiver-treating agent, foams, elastomers, leathers, coatings, building construction, crosslink agent are added to the polyurethane to obtain crosslinked films. In this case, isocyanate terminated polyurethane react with various polyols in different ratio to produce hydroxyl- or isocyanate-terminated urethane prepolymers. Then, the crosslinking reaction is conducted with blocked isocyanate or with various polyols, respectively. The introduction of chemical crosslink-agent changes the structure and chemical, physical, mechanical properties of these croosslinked films and so the morphology becomes often much more complicated.[11–16] Thus, it was found that by varying the chemical structure between incorporating reactants and urethane groups, polyurethanes could be made in a large range of degrees of crosslinking, influencing the physical properties from soft elastomers to rigid and even brittle thermosetting plastics. When polyurethanes are crosslinked, the chemical structures of the polyols, diisocyanate [hexamethylene diisocyanate, diphenylmethane diisocyanate, toluene diisocyanate (TDI)], and chain extender (trimethylol proprane, glycerine, polytetramethylene

TABLE I
Composition of Polyols

	GLY	TMP	DES 550 U
Formula	CH_2—OH CH—OH CH_2—OH	CH_3—CH_2—C—CH_2OH CH_2OH	complex structure
Functionality	3	3	3
% OH	38.00	55.38	11.49
Molecular weight (g mol^{-1})	134.18	92.09	443.8

adipate, pentaerytritol...) have a significant effect on the properties of the resulting material via the presence of Van der Waal's forces and hydrogen bonding. Moreover, depending on the combination of the soft- and hard-segments, the thermal properties are also affected. Indeed, it is well known that the soft segment T_g depends on the hard segment content and on the soft segment molecular weight. Many authors used this thermal parameter as an indicator of the degree of microphase separation. Interestingly, the previous work showed that the T_g of crosslinked polymers was under the room temperature. Associated to the dynamic mechanical properties, this thermal property could be a major asset for some industrial applications.

In this present study and for our industrial application in building conception, an evaluation of the effect of crosslinking introduced ever through the soft segment using a trifunctional polyol [Desmophen (DES) 550 U] and/or through the hard segment using two trifunctional extenders (glycerol (GLY) with various contents and trimethylol propane (TMP) as a fixed constituent) on the crystalline properties of the polyurethane was described. The effects of the chemical crosslink-agent changes on the physical and the morphological properties of the polyurethane films were also reported.

EXPERIMENTAL

Materials

Syntheses were carried out by using TDI, mixture 80/20 of 2,4-TDI and 2,6-TDI (Acros), polypropylene glycol (PPG) with a hydroxy value of 93.5 corresponding to the molecular weight of 1200 (Aldrich). TMP (Acrõs), GLY (Acrõs), and DES 550 U (Bayer) were used to prepare polymer samples with different formulations (Tables I and II). Toluene and butyl acetate were used as received. Dibutyl tin dilaurate (DBTDL, Fluka), used as catalyst, was employed without further purification. The chemical structures of the used polyols are described in the Table I.

Synthesis

Polyurethanes were synthesized using the prepolymer technique.

Preparation of urethane preplymer

To the TDI mixture, diluted in toluene at 70°C, a calculated quantity of TMP was slowly added (Table II). The mixture was then kept at 80°C for 30 min. The calculated amount of PPG and catalyst (DBTDL 0.5 wt %) was then dropped into the solution

TABLE II
Composition of the Formulations

	Composition of reactants in the prepolymer			Film composition			
Films	TDI[a]	TMP[a]	PPG 1200[a]	DES[a]	GLY[a]	% OH DES/GLY	wt % hard segment
I	57.8	12	5.45	19.3	–	100/0	35
II	57.8	12	5.45	14.5	4.8	75/25	38.3
III	57.8	12	5.45	9.65	9.65	50/50	42
IV	57.8	12	5.45	4.8	14.5	25/75	46
V	57.8	12	5.45	–	19.3	0/100	50.7

[a] Mol % was the unit used during the mixing.

of TDI. After adding, the mixture was heated to 90°C for 2 h and then cooled to room temperature. The resultant product was an isocyanate-terminated polyurethane prepolymer in toluene (20%).

Film casting

Five samples with different formulations (Table II) were prepared by mixing and dissolving prepolymer and polyols in a mixture of toluene and butyl acetate (the ratio [NCO]/[OH] was kept constant and nominally equal to 1.0). A little portion of such solution was poured on a smooth surface of glass and allowed to stay at room temperature for 1 day to yield dried films. Crosslinked polyurethane films of thickness within 150 ± 50 μm were obtained. Annealing was carried out on predried samples.

Measurements

Thermal measurements were carried out using a Setaram DSC 111 for the elevated temperatures and TA instruments modulated DSC 2920 [modulated differential scanning calorimetry (MDSC)] to observe the glass transition. MDSC is in fact an enhancement to conventional DSC whereby the total heat flow is separated into reversing (heat capacity) and nonreversing (kinetic) components. The reversing signal contains heat capacity events such as the glass transition and melting. The nonreversing signal contains kinetic events such as crystallization, crystal perfection, and reorganization, cure, and decomposition.

The MDSC experiments were performed after a temperature and a heat flow calibrations by using indium as a standard. The obtained transition temperature and associated heat flow of indium were compared with its literature value (429.75 K, 28.45 Jg^{-1}) to determine the calibration factor. Sample weights of 5 mg were enclosed in aluminum hermetic pans for all MDSC experiments. Each of these samples was first cooled to −60°C with refrigerated cooling system at 10 K/min, equilibrated for 15 min and then heated following the conditions: $T = T_o + q_t + A\sin\omega t$, $T_o = -60$°C, $q = 2$ K min^{-1}, $A = 0.212$°C, $w = 2\pi/P$, $P = 40$ s and over the temperature range from −60 to 100°C. The glass transition temperature was determined as the midpoint of the shift on the heat-temperature curve.

For Setaram DSC, the sample size was 90 mg in quartz tubes. The heating rate was 5°C/min from 30 to 300°C and the sensibility was 250 μV.

For a better understanding of the crystalline properties, one sample was annealed by a program controllable HMO PC-900 high temperature oven. The annealing temperature was from 80 to 120°C, and the annealing time was from 2 to 19h.
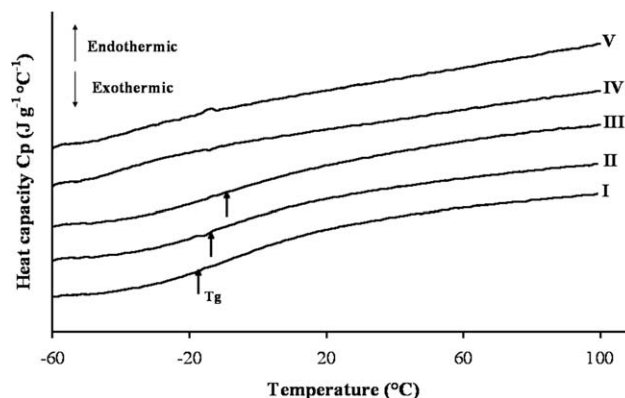
Figure 1 MDSC thermograms of the five films.

A Rheometrics RSA II was used for mechanical dynamical analysis (DMA). The measurements were carried out on dried specimens (35-mm length, 5-mm width, 0.150-mm thickness) at 1 Hz (ε = 0.1%) over the temperature range from −100 to 150°C. Liquid nitrogen was used for subambient testing. Dry nitrogen was used to provide support for DMA air bearing; the excess of nitrogen was released in the DMA oven and served as the purge gas in the DMA tests. The following parameters were obtained: the storage modulus (E′) and the dissipation factor (tan δ) as functions of temperature.

Tensile tests were carried out on five replicates of each material by using an Instron model 1026 testing machine. Several load cells were used (20*N*, 50*N*, and 100*N*) and the cross-head speed was 50 mm/min. These tests were based on the NF T 51-034 and NF ISO 6239 test methods.

The ambient temperature hysteresis behavior was recorded with dog-bone-shaped samples (25 ×4 mm^2). Depending on the films, samples were stretched to a specific percentage strain (50 mm/min cross-head speed) and then brought back to their initial 0% strain conditions at the same cross-head speed. Each sample was subjected to three loading and unloading cycles.

Phase images of the polyurethane samples were captured using a Veeco atomic force microscope (AFM) equipped with a digital instrument Nano-Scope III scanning probe microscope with multimode head and J-scanner. All the measurements were operated in a tapping mode under an ambient condition and high resonance frequencies of these probes were used for imaging (∼ 300 kHz).

RESULTS AND DISCUSSION

Differential scanning calorimetric analysis

MDSC curves obtained for the five samples with different lengths of soft- and hard-segments (films I to V) are shown in Figure 1. This one illustrates the heat capacity curves versus temperature for all of these samples. The soft domain glass transition is
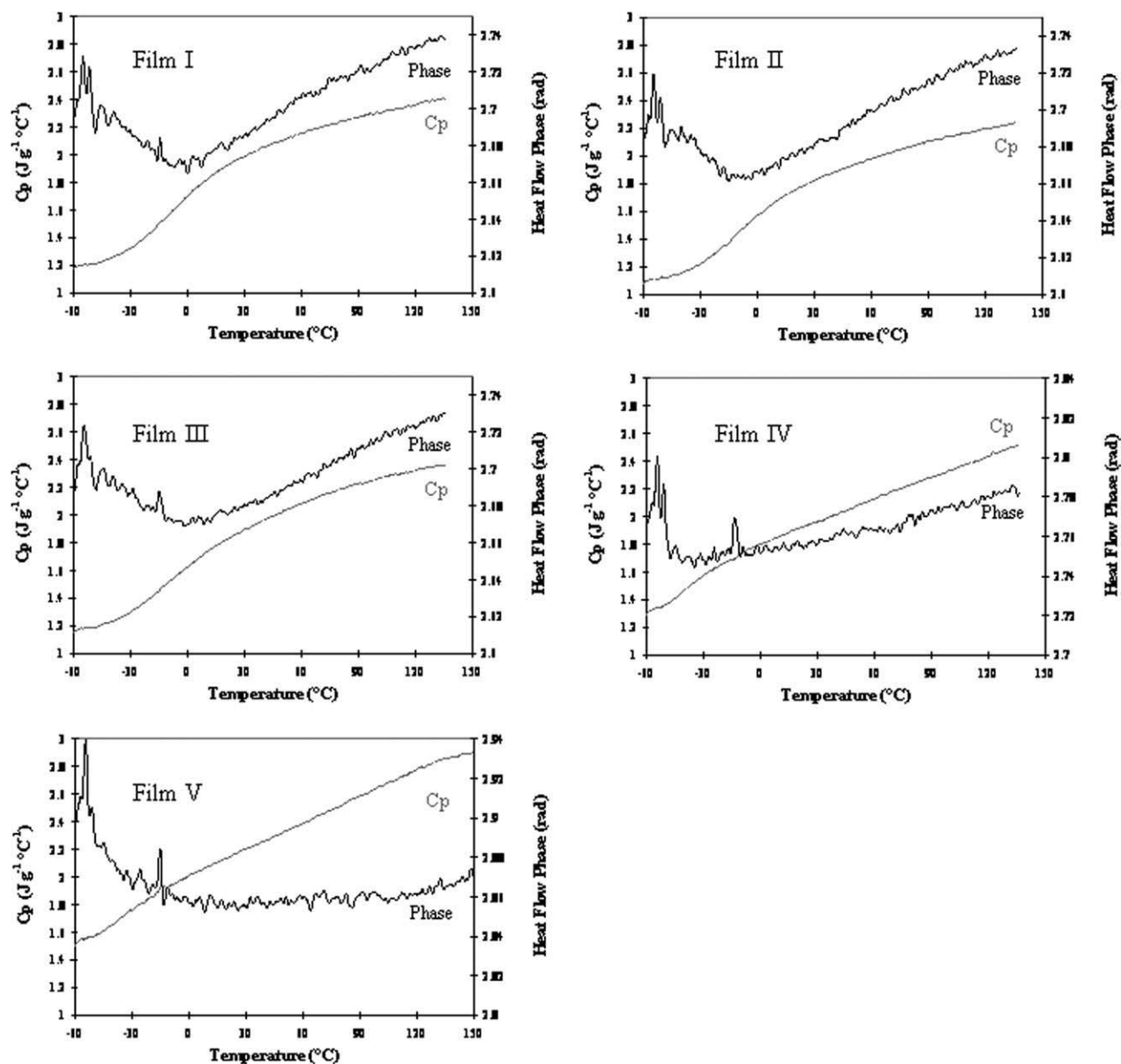
Figure 2 MDSC thermograms of the five films.

easily discernible in samples containing from 0 to 9.65% of glycerol (samples I–III respectively). As contrast, no evident transition was observed for the samples IV and V prepared by incorporation of more than 10% of glycerol into the urethane prepolymer. These observations were in accordance with the data in Figure 2, on which the variation of C_p and those of the heat flow phase depending on the temperature were plotted. These curves clearly show on one hand, an influence of the crosslink-agent chemical structure used in these experiments and on the other hand, an influence on the chemical composition of the obtained materials. Indeed, for films I–III, the C_p variations were well marked and in the same time, a decrease of the heat flow phase occurred, allowing us a fairly accurate assessment of the glass transition temperature. This one remained

relatively constant, suggesting that the penetration of isolated hard segments in the soft phase was limited. Nevertheless, the glass transition temperature of soft segments tended to shift toward higher temperatures with the increase of hard phase contents. For the films IV and V, the shape of the curves were not similar than those obtained for the films I–III. In comparison with these last films, little variations of the C_p parameter were observed for the films IV and V proving the possible existence of a glass transition temperature for each of these two films. Moreover, as shown in Figure 2 for the films IV and V, the decrease of the C_p curves extends over a wide temperature range does not allow the determination of a possible glass transition. From these results, it appeared that the admixture of more than 10% of glycerol into the urethane prepolymer induced
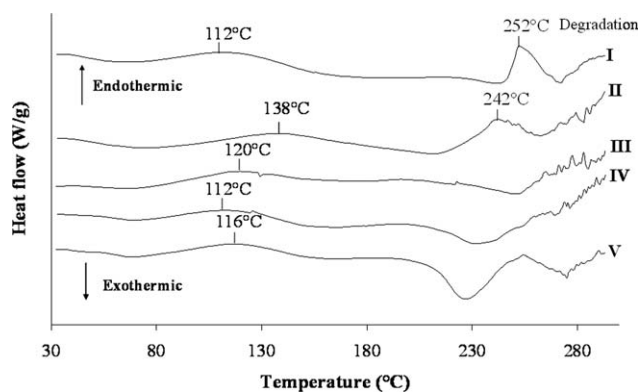
Figure 3 DSC thermograms of the 5 films over the range temperature from −30°C to 300°C.

problems to determine the glass transition of soft segments. Thus, based on these results, we assume that the highest chain mobility was obtained using DES as crosslink agent rather than glycerol. Indeed, the use of DES characterized as a polyether with long and flexible chains is usually used for the formulation of flexible polyurethane in industrial buildings. Thus the mobility chain of the film I was greater than that in the others. Moreover, it appeared that the system obtained after the addition of more than 10% of glycerol was not flexible enough. This finding may be explained by the decrease of molecular mobility which is related to the T_g spreads. For the film II, the crosslinking in the hard phase after adding the glycerol did not really seem to affect the behavior of the soft phase. With regard to the thermogram of the film III (Fig. 2), the admixture of the glycerol into the urethane prepolymer in presence of DES induced a slight spreading of the T_g. There is so a limit related to the glycerol content above which the hard segments affect the transition temperature of the soft segments. As it was the case for the film IV and V, this result could be justified by a gradual incorporation of glycerol in the soft phase.

The DSC thermograms of all of the samples have been plotted on Figure 3. For both of the DSC thermograms of samples I and II, a single endotherm peak was obtained at 252 and 242°C, respectively. These peaks, corresponding to the degree of crystallinity of samples, were attributed to the fusion of crystalline hard segments regions. The endotherm peaks clearly decreased with the increase of the glycerol content. Moreover, for more than 10% of incorporated glycerol into the urethane prepolymer, melting peaks on DSC curves were no longer observed. Interestingly, the DSC curves showed the presence of exothermic peaks, especially, for the films IV and V at around 230°C (Fig. 3). These peaks increased with the glycerol content added into the prepolymer mixture. The investigations of the polymer melting by MDSC interpreted the DSC exothermic peaks that

appeared between 227 and 234°C, corresponding to the melting temperature of soft segments. The nonreversible curves indicated clearly an exothermic peak, suggesting the recrystallization phenomenon during the melting of microcrystalline hard-segments. This process has been already observed in the previous work.[17–19] For the five polyurethane films, the DSC curves showed a little endothermic peaks characterized by temperature values between 112 and 138°C. These peaks may be associated to the different processes, related to the molecular disorder in the hard segments. According to the previous findings, these endothermic peaks may be attributed to the thermal effects associated to the dissociation of the intermolecular bonds and especially to the hydrogen bonds between the –N–H and the C=O groups of the urethane functions[20] and/or to the various disorder forms which occurred in the hard segments of the paracrystalline lattice.[21,22]

With regards to the MDSC and DSC curves, it appeared that the use of DES as chemical crosslinking improves the crystallization process inside the polymer structure. On the other hand, the admixture of high glycerol contents into the urethane prepolymer seems to restrict the formation of the crystalline regions. These findings mean firstly that the crosslinking of the studied urethane polymer by using a short chemical crosslinking is limited and secondly, there was probably a dispersion of the hard segments in the soft-segment matrix. As shown by Petrovic et al.,[16] the high degree of crosslinking induced by the high glycerol contents in the hard segment reduced the mobility of the soft phase and destroyed the crystallinity of the hard phase but they improved heat stability of the hard domains.

For a better understanding of the crystalline properties of the sample I, subsamples were made and the DSC curves of these subsamples, annealed at several temperatures and cure times [80°C (2 h), 80°C (4 h), 80°C (19 h), and 120°C (4 h)] were plotted in Figure 4. The DSC curves related to the
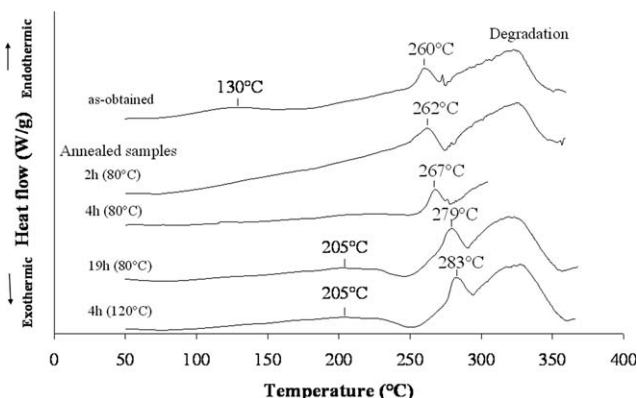

Figure 4 DSC thermograms of polyurethane I after annealing under several conditions.
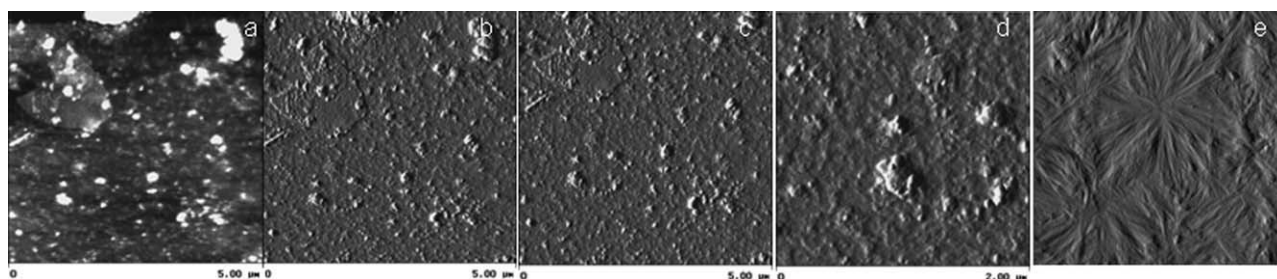
Figure 5 AFM topographic images for the non heat-treated film I (a) and annealed samples: 2 h, 80°C (b); 4 h, 80°C (c); 19 h, 80°C (d) and spherulite in this annealing conditions (e).

subsamples annealed at different time showed that the melting behavior of crystalline segments is affected by the thermal treatment. The characteristic growth and shift of the hard domain melting endotherms with annealing is observed for all subsamples and based on our experiments, the results show that the melting temperature of the sample I depend upon the time the sample was previously annealed, and then on the heating rate applied. The melting temperature values depend finally on the annealing history of the sample and may be attributed to the recrystallization phenomenon during the heating of the samples and/or the possible reorientation and complete organization during the cooling made from the high temperature.[23] In comparison with the DSC curve obtained for the sample I before annealing, those related for 19 h and 4 h have a small endothermic peak at 205°C. These peaks may be attributed to the dissociation of domains containing long range order and therefore may contribute to the possible formation of imperfect crystal structures for which small exothermic peaks were observed around 250°C. According to the previous work, results suggest that annealing induced ordering is an intradomain phenomenon neither associated with the interphase between domain, or necessary dependent on the chain architecture of the polyurethane.[24,25]

The AFM topographic image for the nonheat-treated film I and annealed samples are shown in Figure 5. At first glance, it appears many irregularly crystalline regions (white) at random on the surface of the film I before annealing (a). For the annealed samples, it can be observed some crystalline regions for which an orientation and a rearrangement of the hard segments probably occurred due to the freedom of the chain segments on the surface.[26] For the annealed sample at 80° and 19 h, a distinguish spherulite structure was observed with a very clear contour of each "petal." According to the previous findings, a plausible explanation of this observation is that in the case of heat-treatment, the chain segments of polyurethane films have access to reorient or to rearrange fully during the cooling of elevated temperature.[23] Thus, the annealing process would allow the aggregation of the hard segments to form

hard-segment domains in which a relatively perfect crystalline region develops.

Dynamic mechanical analysis

Dynamic mechanical experiments provide information on first- and second-order transitions, T_m and T_g respectively, phase separation and the mechanical behavior of polyurethanes. Figure 6 illustrates the dynamic mechanical behavior of samples I, III, and V and shows clearly the morphological modifications of the studied polymer structure. The evolution curves of the storage modulus E′ versus temperature associated to the three films are shown in Figure 6(a). For the films I and III, modulus E′ decreased at least three orders of magnitude as temperature increased from −30 to 110°C and higher than 110°C a stabilization of this modulus value occurred,
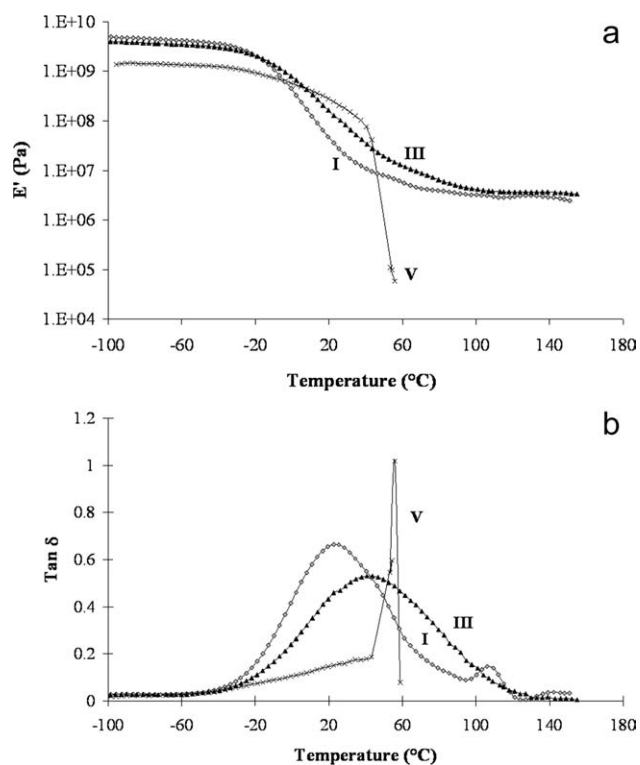

Figure 6 DMA curves of polyurethanes **I**, **III** and **V**.

TABLE III
T_g Values Obtained by MDSC and DMA for the Films I, III and V

Films	T_g[a] (°C)	T_g[b] (°C)	ΔT_g[c] (°C)	ΔT_g[d] (°C)
I	−1.5	7.5	0	8.5
III	5.5	22	14.5	16.5
V	−15–15	52	44.5	37–67

[a] T_g was determined by MDSC.
[b] T_g was determined by DMA.
[c] $\Delta T_g = T_g$ (DMA) for the films III or V − T_g (DMA) for the film I.
[d] $\Delta T_g = T_g$ (DMA) − T_g (MDSC).

indicating probably the presence of physical crosslinks (hydrogen bonding and/or crystallization between hard segments) in the samples I and III.[4] The plateaus, shown in Figure 6(a), are not very different but we may consider that the slightly decreasing of the modulus curve for the film I (from 140 to 155°C), is related to the low hard segment content while for the film III, the plateau extended to about 160°C, implying a highest hard segment content, for which domains can be amorphous or partly crystalline. Another factor which affects the mechanical properties of polyurethanes is the dispersion of the soft- and hard-segment lengths.[27] Compared to the thermal characteristic of the film III, the lower and sharper T_g in the film I, indicate that there was more soft segment phase in the resulting crosslinked polyurethane. In contrast, for specimen V, the modulus dropped abruptly from 40 to 55°C and no plateau was observed. Interestingly, the difference between this film and the two others (I and III) was the presence of a large amount of glycerol, the short crosslink agent used in this study. Li et al. (1996) explained the dropping of the modulus curve in polyurethane by the existence of a limit of about 10% by weight, below which the formation of hard segment domains became difficult for films having low hard segment content and short hard segment length.[6] With regard to the ratio of hard segment (50.7%, Table II) and the results obtained by DSC, the structure of the film V appears to be a linear amorphous structure material with probably the presence of amorphous hard segment domains. The dissipation factor of the three films was plotted in Figure 6(b). The tan δ versus temperature curves display loss peaks associated with the glass transition and damping capacity of the soft domains. The sharpness and height of the damping peaks give information about the mobility of the molecular chains[28] and relates to the degree and strength on chemical bonds in the polymer structure.[29] The curves in this figure show that an increase of the short crosslink agent (glycerol) content induces a shift of the glass transition peak to a higher tempera-

ture. In comparison with the curves of the film III, the sample I display the most prominent damping peak. As shown by Martin et al. (1996), the incorporation of large amount of DES, inducing flexible linkages of the soft domains, could improve damping. With regard to the DSC curve, this results may be explained the degree of the crystallinity of the soft domain in the film I. Moreover, for this film, a second peak was obtained at about 110°C probably due to a second type of soft segment melting. For the film V, a sharp damping peak appears at about 56°C. This peak attests a decrease of the chain mobility which may be explained on one hand, by the presence of large amount of the short crosslink agent inducing an increase of crosslink density to produce crosslinked polymer and/or on the other hand, by
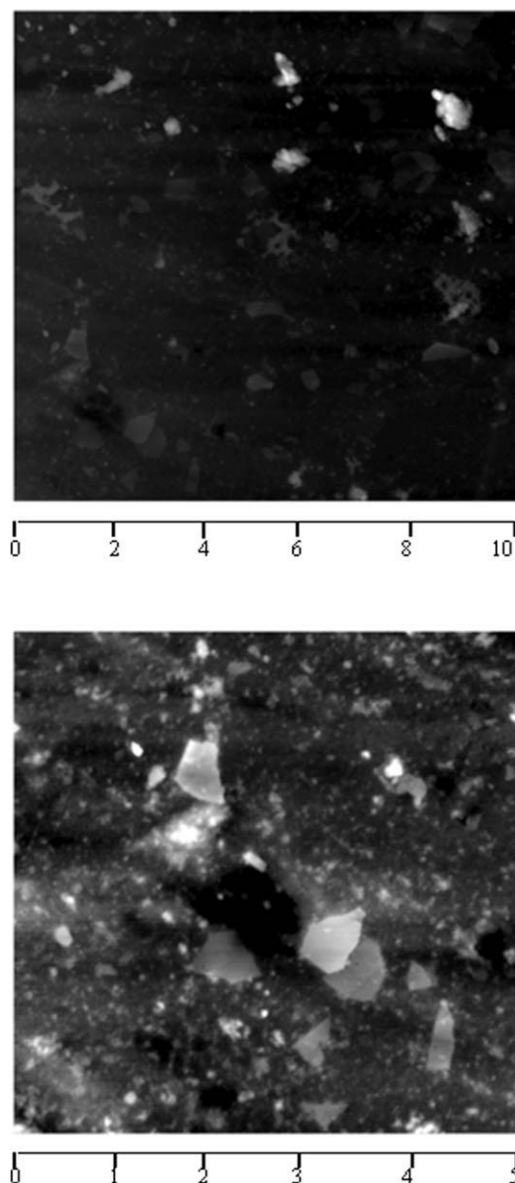

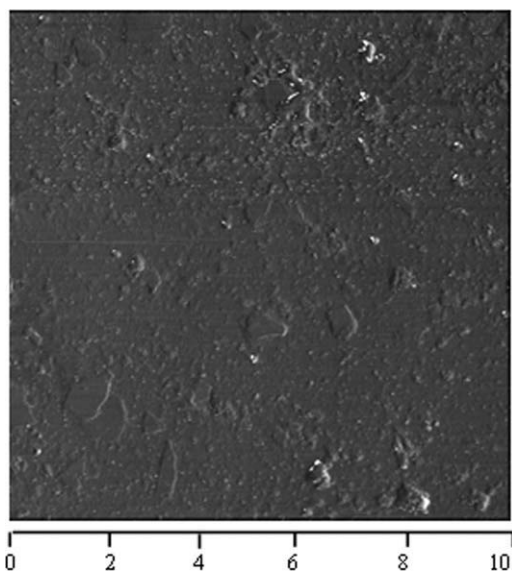**Figure 7** AFM topographic images (10×10 mm) and (5×5 mm) for the film **I**.

Figure 8 Contrast phase AFM topographic images (10×10 mm) of the film **I**.

Figure 9 AFM topographic images (10×10 mm) and (5×5 mm) for the film **V**.

the presence of shorter soft- and hard-segments than those existing without glycerol. A third explanation of this phenomenon may be given by the position of damping peaks, which provide information about the degree of phase separation in polyurethane films. As shown in the Table III, the difference between the T_g of films III and V and the T_g of film I (i.e., ΔT_g) increased and this, with the increase of the glycerol content inducing probably an increase of the hard block numbers dissolved in the soft phase. Consequently, with regard to the film I used as a control film, the phase separation between soft- and hard-segments inside the sample matrix III and V were less.

The transition temperatures (T_g), as indicated by the tan δ peaks, were higher than those detected by MDSC. It should be noted that the DMA technique generally provides higher T_g values (usually up to 10°C higher) than those obtained by MDSC. This difference can be explained by the nature of tests for which T_g measurements from MDSC depend on the modulation oscillation frequency, and T_g measurements using DMA depend on the stress/strain oscillation frequencies.[30] In our study, T_g values from DMA are much higher than T_g from the DSC measurements and the ΔT_g increase with the amount of glycerol added (Table III). With a lesser extent, Sutrismo (2005) obtained difference between transition temperatures higher than 10°C for both studied polyurethane polymers.[31] According to its study, this difference represent that at the beginning of a glass transition process heat capacity increases as free volume increases, even if there is no significant change in kinetics. Applying this theory to the studied films, the additional of the short crosslink agent (glyc-
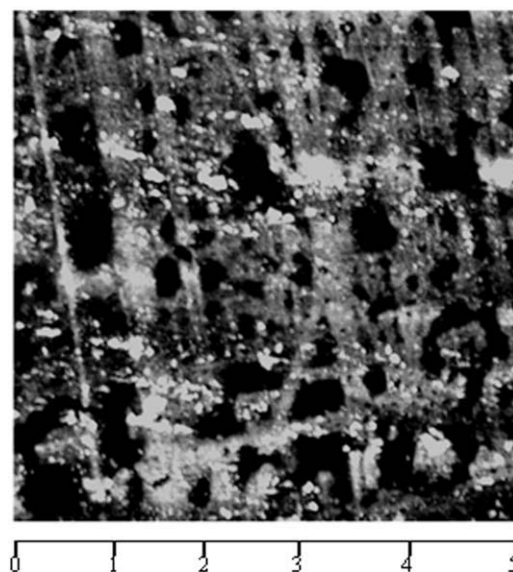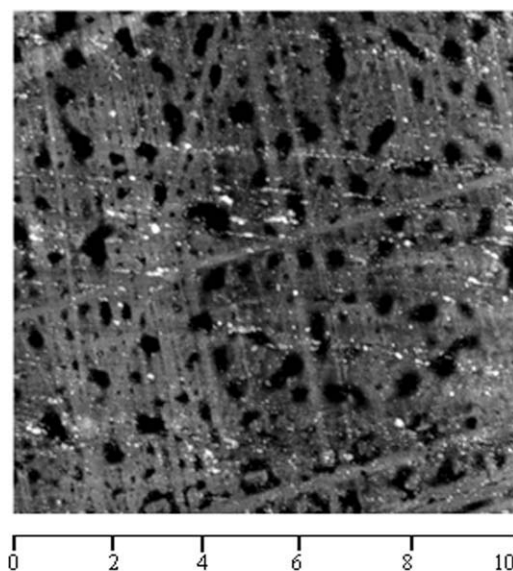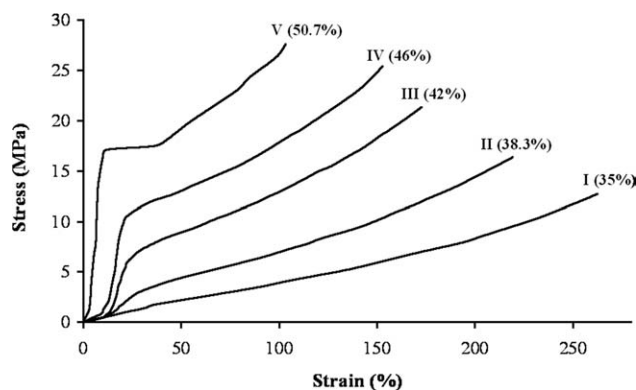

Figure 10 Stress-strain curves for all compositions. The DES / GLY ratios are: (I) 100/0; (II) 75/25; (III) 50/50; (IV) 25/75; (V) 0/100 (wt.% of hard segment is also indicated).

TABLE IV
Variation of Tensile Properties With Formulation

DES/GLY ratio	100/0	75/25	50/50	25/75	0/100
E (MPa)	4.4	15.4	63	117.4	260
σ_f (MPa)	12.7	16.4	21.4	25.4	28
ε_f (%)	262	219	173	153	103

erol) increases the free volume inducing much time for the polymer to reach an equilibrium condition before it starts to loose elasticity property and to activate small segmental mobility. Thus, the highest T_g value for the film V suggests that the soft segment cannot move as easy as in the film I and III, for which the little ΔT_g may be explained by the presence of crystalline domain or micro domain, known to reduce the soft segment mobility. The behavior of the three studied film is so highly influenced by the glycerol content and may be interpreted on the basis on the changes in free volume and chain mobility as shown in a previous finding.[16] If the DES seemed to undergo microphase separation into hard- and soft-domains, it appeared that the short crosslink agent (glycerol) induce the dispersion of hard domains, increasing the miscibility of hard- and soft-segments, and reduce the mobility of the soft phase by chemical crosslinking.

Surface crystalline characteristics investigated by atomic force microscopy

The surface morphology down to the nanoscale in particular, the three-dimensional image, can be obtained by tapping-mode AFM. Lots of studies have been conducted on the crystalline characteristics of the polyurethane surface[32–35] but no much study has been yet reported on the polymers obtained by reaction between polyols and TDI mixture.[23] The AFM topographic images (10×10 μm^2) and (5×5 μm^2) for the films I are shown in Figure 7. At first glance, it appears many irregularly crystalline regions (white) at random on the surface of the film I. A smaller scale

scan shows that the "stones" are finally crystalline regions. Phase contrast imaging of this polyurethane film (Fig. 8) indicates clearly the presence of dispersed crystalline regions inside a flexible rubbery matrix. This result was confirmed by the melting point value at 252°C determined by DSC (Fig. 3). As contrast, no crystallinity was observed inside the structure of the polyurethane film V (Fig. 9). The difference between the structures of the films I and V can be explained by the addition of glycerol as a short crosslink agent. In the last film, the sizeable content of the short-chains triol seemed to prevent the separation of hard- and soft-segments inducing a decrease of the chains mobility and an impossible rearrangement of the hard segments to form crystalline region. Without glycerol (film I), it appeared that the flexibility of chains was highest. Thus phase separation steps between the soft- and hard-segment occurred and aggregation of hard segments took place to form hard segment domains in which crystalline region have been developed.

Tensile stress-strain behavior

Tensile tests were performed to examine the effects of polyurethane formulation ratio DES/GLY on the tensile properties and particularly to note the extent of hard phase connectivity and mechanical performance of the polyurethanes with respect to elongation at break and ultimate tensile strength. Figure 10 and Table IV show that the Young's modulus and the fracture stress increase as the glycerol content increase. Results showed clearly that materials IV and V had a distinct yield point at room temperature. This point led us to postulate that for the materials IV and V, there is a very well percolated hard phase throughout the soft matrix. The obtained yield point at room temperature was so attributed to the breakup of the percolated hard phase as it was the case for other materials.[36,37] In fine, materials I and II display typical elastomeric stress–strain curve whereas materials III–V exhibit more a thermoplastic behavior. The variation of properties can be
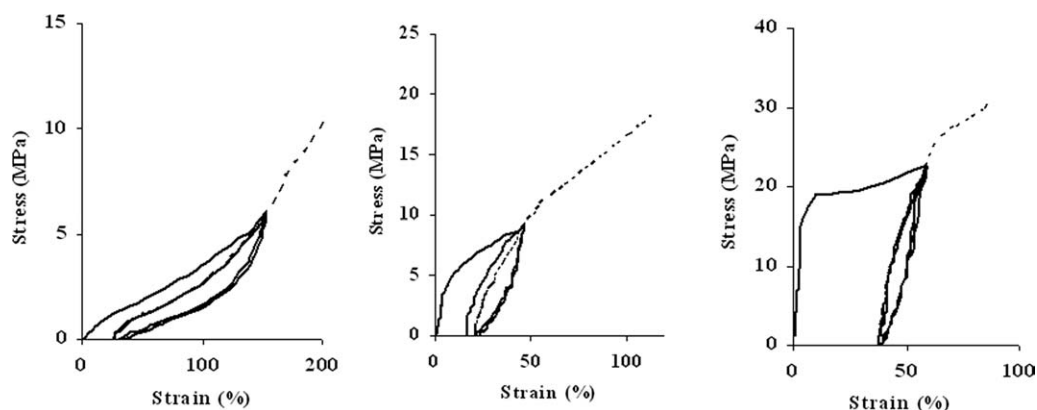

Figure 11 Stress-strain curves for films **I**, **III** and **V**. Three tensile cycles without stop.
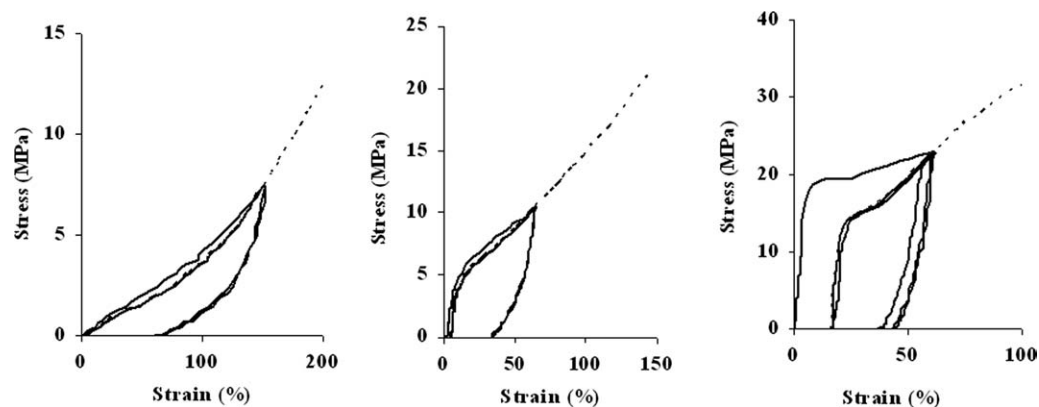
Figure 12 Stress-strain curves for films **I**, **III** and **V**. Three tensile cycles with 5 minutes stop between each cycles.

explained by the use of two structural different triols (DES in the soft phase and glycerol in the hard phase), by the increase of the percentage of hard segments and crosslink density in the materials and by the change in domain morphology.

We also examined the "shape" memory of the materials I, III, and V. The recover capacity of each material is shown in Figures 11 and 12. Higher the percentage of hard segment, higher the hysteresis. The differences appear clearly between the three materials. Sample I behaves like an elastomeric material whereas sample V exhibits a viscoelastic behavior.

CONCLUSION

It is clear that the crosslink agent used, either DES, trifunctional polyol or glycerol trifunctional extender is the main factor determining not only the crosslink density but also on the one hand, the structure and the morphology of polyurethanes and on the other hand, their thermal and their dynamic mechanical properties. In presence of DES and trimethylolpropane, some crystalline regions between hard segments were observed in the soft phase. It has been found that the crosslink density increased regularly with the glycerol contents, used as a short crosslink agent. At higher hard segment levels, the mobility of the soft phase was reduced and chemical crosslinks through the hard segment were found to destroy the cristallinity of the hard phase, improving the heat stability of the hard domains.

References

1. Allport, D. C.; Janes, W. H. In Block Copolymers; Wiley: New York, 1973, p 443.
2. Cooper, S. L.; Tobolsky, A. V. J Appl Polym Sci 1966, 10, 1337.
3. Lelah, M. D. In Polyurethanes in Medicine, Cooper, S. L., Eds.; CRC Press: Boca Raton, Florida, 1973, p 225.
4. Li, F.; Hou, J.; Zhu, W.; Zhang, X.; Xu, M.; Luo, X.; Ma, D.; Kim, B. K. J Appl Polym Sci 1996, 62, 631.
5. Zdrahala, R. J.; Gerkin, R. M.; Hager, S. L.; Critchfield, F. E. J Appl Polym Sci 1979, 24, 2041.
6. Martin, D. J.; Meijs, G. F.; Renwick, G. M.; Gunatillake, P. A.; McCarthy, S. J Appl Polym Sci 1996, 60, 557.
7. Paul, C. J.; Nair, M. R. G.; Neelakantan, N. R.; Koshy, P.; Idage, B. B.; Bhelhekar, A. A. Polymer 1998, 39, 6861.
8. Paul, C. J.; Nair, M. R. G.; Neelakantan, N. R.; Koshy, P. Polym Eng Sci 1998, 38, 440.
9. Sukumar, P.; Jayashree, V.; Gopinathan Nair, M. R.; Nair, M. N. R. J Appl Polym Sci 2009, 111, 19.
10. Chen, R.-S.; Cheng, Y.-L.; Chang, K.-W. J Appl Polym Sci 2009, 111, 517.
11. Hu, X.; Young, R. J Plast Rubb Proc Appl 1989, 12, 113.
12. Lagasse, R. R. J Appl Polym Sci 1977, 21, 2489.
13. Russo, R.; Thomas, E. L. J Macromol Sci Phys 1983, B22, 553.
14. Yang, C.-P.; Wu, W.-L. J Appl Polym Sci 1983, 28, 2509.
15. Van Bogart, J. W. C.; Gibson, P. E.; Cooper, S. L. J Polym Sci 1983, B21, 65.
16. Petrovic, Z. S.; Javni, I.; Divjakovic, V. J. Polym Sci B Polym Phys 1998, B36, 221.
17. Dickie, B. D. Thermochim Acta 1997, 304, 347.
18. Verdonck, E.; Schaap, K.; Thomas, L. C. Int J Pharm 1999, 192, 3.
19. Wang, L.-F. Eur Polym J 2005, 41, 293.
20. Clough, S. B.; Schneider, N. S. Macromol 1968, B2, 553.
21. Seymour, R. W.; Cooper, S. L. Macromol 1973, 6, 48.
22. Srichatrapimuk, V. W.; Cooper, S. I. J.; Macromol Sci Phys 1978, B15, 267.
23. Xu, M. X.; Liu, W. G.; Wang, C. L.; Gao, Z. X.; De Yao, K. J Appl Polym Sci 1996, 61, 2225.
24. Darby, R. T.; Kaplan, A. M. Appl Microbiol 1968, 16, 900.
25. Hunter, S. K.; Gregonis, D. E.; Coleman, D. L.; Andrade, J. S.; Kessler, T. Trans Am Soc Artif Inter Organs 1982, 28, 473.
26. Meyers, G. F.; Dekoven, B. M.; Seitz, J. T. Langmuir 1992, 8, 2330.
27. Ng, H. N.; Allegrezza, A. E.; Li, F.; Seymour, R.W.; Cooper, S. L. Polymer 1973, 14, 255.
28. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites, 2nd ed.; Marcel Dekker: New York, 1991, pp 240.
29. Tregub, A.; Ng, G.; Sorooshian, J.; Moinpour, M. Thermochim Acta 2005, 439, 44.
30. Simon, S. L. Therm Act 2001, 374, 55.
31. Sutrismo, W. Indian J Phys 2005, 16, 53.
32. Lee, J.-Y.; Lee, W.-J.; Park, E.-J.; Bang, H.-B.; Rhee, B. K.; Jung, C.; Lee, S.-M. Bull Korean Chem Soc 2003, 24, 1727.
33. Das, S.; Yilgor, I.; Yilgor, E.; Inci, B.; Tezgel, O.; Beyer, F. L.; Wilkes, G. L. Polymer 2007, 48, 290.
34. Ong, Q. K.; Sokolov, I.; Chechik, N.; James, D. Polym Mater Sci Eng 2005, 92, 100.
35. Tang, D.; Wu, X.; Qiang, L. J Mater Sci Technol 2007, 23, 423.
36. Abouzhar, S.; Wilkes, G. L.; Ophir, Z. Polymer 1982, 23, 1077.
37. Sheht, J. P.; Klinedinst, D. B.; Wilkes, G. L.; Yilgor, I.; Yilgor, E. Polymer 2005, 46, 7317.