

# Physical Characterization and Rheological Behavior of Polyurethane/Poly( $\epsilon$ -caprolactone) Blends, Prepared by Solution Blending Using Dimethylacetamide

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**ABSTRACT:** Blending effects of thermoplastic polyurethane based on polycaprolactone diol, PU (PCL diol), and poly ( $\epsilon$ -caprolactone) (PCL) on the rheological properties and morphological behavior of the solvent-cast blends were investigated by parallel plate rheometer. The amount of PCL was varied from 20 to 50% by weight. Fourier transform infrared (FTIR) results showed existence of hydrogen bonding in PU/PCL blends. From FTIR, we also found the increase of PCL composition tends to reduction of intermolecular hydrogen bonding and enhancing of microphase separation in blends. Differential scanning calorimetry (DSC) indicated that these blend systems are partially misci-

ble. Based on rheological characterization, decrease can be seen in the moduli, zero shear viscosity and plateau modulus of blends, as compared with net PU. Using Cole-Cole plots and composition dependencies of  $\eta_0$  and the other viscoelastic functions expressed variation of morphology of blends due to increase of PCL content. Frequency sweep tests on PU/PCL (80/20) at five temperatures showed validity of time-temperature superposition in this blend. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** PU/PCL blend; rheology; solution blending; time-temperature superposition

## INTRODUCTION

Polyurethanes are phase separated block copolymers, which are composed of two segments. One segment, called the hard segment, is rigid, while the other, the soft segment, is elastomeric. In polyurethanes, the soft segment is prepared from an elastomeric long-chain polyol, generally polyester or polyether, but other rubbery polymers end-capped with a hydroxyl group could be used. The hard segment is composed of the diisocyanate and a short-chain diol called a chain extender. The hard segments have high interchain attraction due to hydrogen bonding between the urethane groups. In addition, they may be capable of crystallizing. The soft elastomeric segments are held together by the hard phases, which are rigid at room temperature and act as physical cross-links.<sup>1</sup> It is well-known that there is always a microphase separation in segmented polyurethanes.<sup>2</sup> For the first time, Ajili used of these properties of polyurethanes in biomaterial technology. In their research, the hard phase of PU was 4, 4'-methylenediphenyl diisocyanate (MDI) and 1,4-

butanediol (BDO) segments and its soft phase was made of PCL diol. It was found that polyurethane/polycaprolactone (PU/PCL) blend could act as a proposed material for shape memory stents because of their self-expansion in the range of body temperature. The shape memory effects of Polyurethane copolymer based on poly( $\epsilon$ -caprolactone) diol, which was melt blended with PCL in different ratios of 20, 30, 40, and 50 wt%, was examined. Blends showed shape memory effects with recovery temperatures of around the melting temperature of PCL in the blends. The melting behavior of the PCL in the blends was strongly influenced by composition. In PU/PCL blends, there are also two phases. One phase is hard segments of PU and the other one is composed of miscible domain of PCL and PCL diol. It is believed that because of microstructural similarity of PCL with the soft segments of PU, some parts of PCL are dissolved in the PU to form a "new matrix" of lower modulus than pure PU. The chains of the higher molecular weight of component PCL compared to PCL blocks in PU, prefer to form micelles (droplets) instead of dissolving in those with lower molecular weight. Therefore, the rest of PCL is dispersed in this new matrix with a coarse morphology. In this case, the blend system is semi miscible or "partially miscible."<sup>3,4</sup>

Based on composition, temperature, and pressure, a partially miscible polymer blend can be

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homogeneous or heterogeneous. These blends have different internal structures and thus show different rheological behavior. The homogeneous blends exhibit simple thermorheological behavior and time temperature superposition (TTS) principle is applicable for them. Then, their rheological functions at different temperatures can fall on the same curve. But, the elasticity in the terminal region for phase-separated blends makes the TTS principle invalid for them and shows thermorheological complexity.<sup>5</sup> From this point of view; miscible polymer blends play different roles. Blends with specific interactions such as ionic or dipole-dipole interaction and hydrogen bonding, follow the TTS principle. In miscible blends with weak interactions, presence of concentration fluctuations or dynamic heterogeneity tends to broaden the glass transition temperature and then failing the TTS principle.<sup>6-9</sup>

With the exception of Ajili's work, there is no research about PU/PCL blends. In that work, the dynamic rheological properties of PU/PCL blends, prepared by melt blending, was theoretically analyzed using modified Palierne model.<sup>3</sup> We were interested in studying rheological behavior of PU/PCL blends preparing by solution blending. So, PU and PCL were blended using dimethylacetamide solvent. Then physical characterization and rheological behavior of PU/PCL blends are studied by frequency sweep, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) tests.

## EXPERIMENTAL

### Materials and blend preparation

Polyesterurethane (LPR2102-85 AE) was delivered from Coim Co. (Italy) with a density of 1.16 g/cm<sup>3</sup>. This polyurethane consists of hard segments based on MDI and BDO and soft segments of polycaprolactone with a  $M_n$  of 2000 g/mol. Polycaprolactone (PCL) was obtained from Sigma-Aldrich Co. (Germany) with a  $M_n$  of 42,500 g/mol, a density of 1.145 g/cm<sup>3</sup> and a melting point of 60°C. PU and PCL were dried in a vacuum oven at 100°C for 24 h and 40°C for 5 h, respectively. Dimethylacetamide with density of 0.94 g/cm<sup>3</sup> was purchased from Merck Schuchardt OHG (Germany). PU/PCL blends were produced via a solution blending method, using dimethylacetamide as a solvent. The solution was prepared by stirring the PU mixture for 6 h at temperature of 60°C and then PCL was added to it. After the PU/PCL solutions were blended by stirring for about 7 h, solutions were cast on the glass plates in an oven at 60°C for 28 h. To ensure total elimination of solvent, the films were then dried in a vacuum oven at 70°C until a constant weight was

obtained. We made PU/PCL blend ratios of 100/0, 80/20, 70/30, 60/40, 50/50, and 0/100 by weight.

### Differential scanning calorimetry

A differential scanning calorimeter (DSC) (Mettler Toledo DSC-822) was used to determine the thermal properties of the PU/PCL blends. Sub ambient temperatures were reached using liquid N<sub>2</sub> to cool the DSC cell. In all cases, samples were sealed in aluminum pans with a sample weight ranging of 5–6 mg.

The following heat treatments were carried out.

The samples were heated from –100°C to 250°C (first heating scan) at a rate of 10°C/min in order to remove prior thermal histories; subsequently, they were cooled to –100°C at a rate of 10°C/min. A second heating scan was then performed at the same first scan conditions.

### FTIR characterization

To detect hydrogen bonding in the blends, infrared spectra of polymer blend films were determined using a Bio-Rad FTS-40A spectrometer operated with a dry air purge.

### Morphological characterization

The morphology of the blend was characterized by scanning electron microscopy (SEM) using a Philips, model XL 30 microscope. The samples were fractured in liquid nitrogen and then covered with gold. To improve the contrast, fractured surfaces were etched using acetone at 40°C for 6 h.

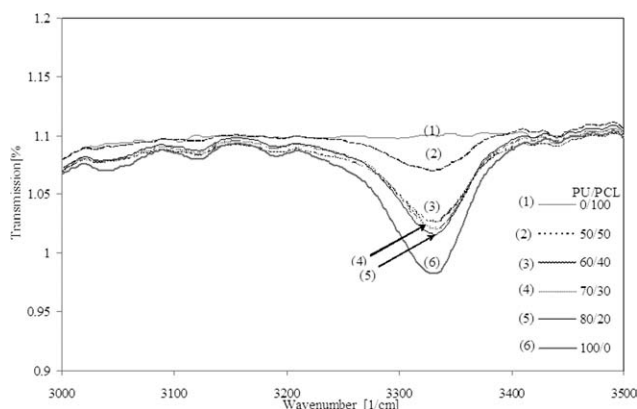
### Rheological measurements

The rheological measurements were performed with a stress/strain-controlled rheometer, UDS 200 made by Paar Physica. The experiments for blends were carried out using disk type parallel plates with 25 mm diameter and 1 mm gap at 200°C. Frequency sweeps were carried out at frequency range of 0.1–500 rad/s and strain 5% (linear viscoelastic region).

## RESULTS AND DISCUSSION

### Molecular interactions in PU/PCL blends

As reported in experimental section, thermoplastic polyurethane is a block copolymer containing hard and soft segments. The hard segments contain C=O and N–H groups that could form hydrogen bonding. PCL and the soft segments of PU also have C=O groups. So hydrogen bonding could form between hard and soft segments or PCL chains. Here two infrared stretching vibration absorption regions are important: the N–H band (3000–3500

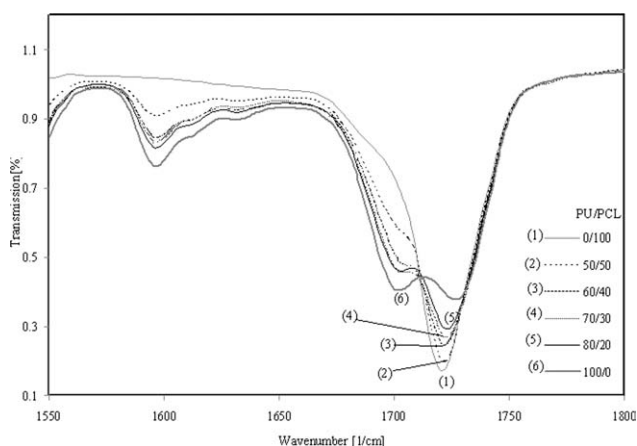


**Figure 1** FTIR spectra at the region of 3500–3000  $\text{cm}^{-1}$  for PU/PCL blends.

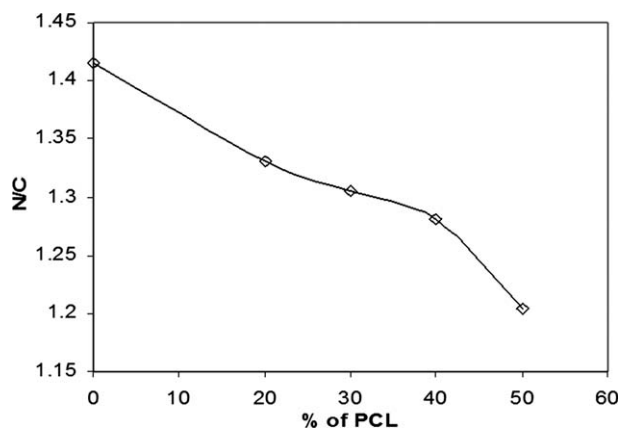
$\text{cm}^{-1}$ ) and C=O band (1500–1800  $\text{cm}^{-1}$ ). Figure 1 shows the FTIR spectra of the pure PU and its blends with PCL at the region of 3000–3500  $\text{cm}^{-1}$ . It can be seen that the hydrogen bonded N–H group appeared at 3330  $\text{cm}^{-1}$ ,<sup>10,11</sup> but the small absorption peak of free N–H group at 3419  $\text{cm}^{-1}$  overlapped with one peak of PCL, which is not reliable. The concentration of hydrogen bonded N–H group decreases with an increase of PCL content.

Figure 2 shows the FTIR spectra of the pure PU and its blends with PCL at the region of 1500–1800  $\text{cm}^{-1}$ . Free C=O group is observed at wave number of 1725  $\text{cm}^{-1}$  and the hydrogen bonded one appears at 1702  $\text{cm}^{-1}$ .<sup>10,11</sup> Increasing of PCL content causes the enhancement of free C=O group absorption and decrease of hydrogen bonded one. This results show that miscibility of blends decreases with increase of PCL composition.

The hard and soft segments of PU are thermodynamically immiscible. Therefore there is microphase separation between hard and soft segments in PU. An important peak in the FTIR spectra for PU and



**Figure 2** FTIR spectra at the region of 1550–1800  $\text{cm}^{-1}$  for PU/PCL blends.

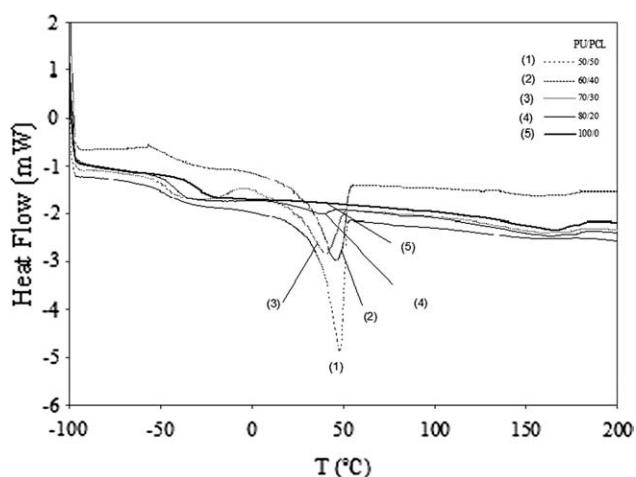


**Figure 3** The relative intensity of absorbance at 3120  $\text{cm}^{-1}$  (N) to that one at 1596  $\text{cm}^{-1}$  (C).

its blends is the absorption peak of bending vibration of N–H group in hard segment at 3120  $\text{cm}^{-1}$  (see Fig. 1). The intensity ratio of this peak over stretching vibration of C=C in benzene ring of urethane at 1596  $\text{cm}^{-1}$  is a criterion for measuring microphase separation in pure PU and its blends.<sup>3,12,13</sup> Wang has believed that increasing of phase separation amount tends to the reduction of the ratio of N/C groups at surface and bulk region of PU.<sup>14</sup> As observed in Figure 3, an increasing of PCL composition in the blend reduces the ratio of N/C and subsequently increases the phase separation in PU/PCL blends. This behavior is because of dissolving of PU soft segments in PCL.<sup>3</sup>

### Thermal behavior of PU/PCL blends

Figures 4 and 5 show the DSC cooling and heating thermograms, respectively. Crystallization and melting temperatures ( $T_c$ ,  $T_m$ ) of the soft segments of blends, compared with the pure PU, are reduced by the increase of PCL. Nearly, the same trend can be



**Figure 4** DSC cooling thermograms for PU and its blends.

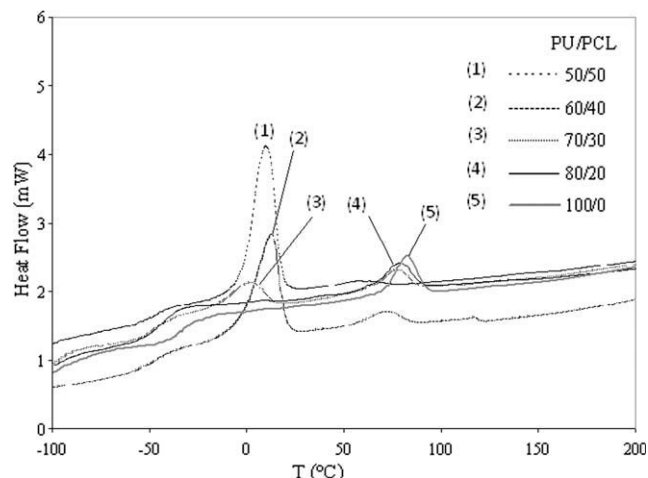


Figure 5 DSC heating thermograms for PU and its blends.

observed for the hard segments. This means that the blending of PCL with PU suppressed crystallization of PCL. Existence of a single glass transition temperature in the DSC thermograms and closing  $T_m$  and  $T_c$  of hard and soft segments together by increasing the PU composition (or decreasing the PCL composition) suggest that this blend is partially miscible. Chan et al. reported the same result for PCL/PS blend. In immiscible blends, the second component affect on primary nucleation of the crystallizing component. But in the miscible blends, the energy barrier for the formation of a critical nucleus in the blends compared with homopolymer, is greater. Therefore, nucleation activity of heterogeneous nuclei in the blends generally decreases with increasing the concentration of a second polymer in the blend.<sup>15</sup> Therefore, according to the results of  $T_c$  of PCL shown in Figure 4, the PU deactivated the crystallization of PCL in the PU/PCL blend. From the results of  $T_c$  and  $T_m$ , partially miscibility of PU/PCL blend is suggested.

It is known that PU and PCL form hydrogen bonding. Some of researchers believed that width of glass transition temperature ( $\Delta w_{T_g}$ ) are a measure for detecting specific interactions between blend components. As mentioned in literature, the broadness of  $T_g$  is related to the concentration fluctuation and dynamic heterogeneity. We calculated the width of  $T_g$  by  $\Delta w_{T_g} = T_{gf} - T_{gi}$ . In this equation,  $T_{gi}$  and

TABLE 1  
 $T_{gi}$ ,  $T_{gf}$ ,  $T_g$ , and  $\Delta w_{T_g}$  for PU and PU/PCL Blends

Amount of PCL (%)	$T_{gi}$ (°C)	$T_g$ (°C)	$T_{gf}$ (°C)	$\Delta w_{T_g}$ (°C)
0	-37.96	-29.79	-21.62	16.34
20	-48.08	-40.15	-32.22	15.86
30	-52.35	-45.44	-38.53	13.82
40	-56.06	-45.89	-35.72	20.34
50	-58.39	-47.42	-36.45	21.94

$T_{gf}$  are the onset and the end points of glass transition. As observed in Table I, in the high concentration of PCL compared with low one,  $\Delta w_{T_g}$  is broaden. This is in agreement with the FTIR spectra.

The equation presented by Kwei quantified the relationship between  $T_g$  and hydrogen bonding in the polymer blends:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \quad (1)$$

Where  $w_1$  and  $w_2$  are weight fractions of the compositions,  $T_{g1}$  and  $T_{g2}$  represent the corresponding glass transition temperatures, which the subscripts 1 and 2 refer to PCL and PU, respectively.  $k$  and  $q$  are fitting parameters. Kwei suggested that  $q$  is a measure for determining the strength of specific interactions in the blend and reflecting a balance between the breaking of the self-association and the forming of the interassociation hydrogen bonding. The hydrogen bonds in one component, PU in this study, are called self association hydrogen bonds. The positive and negative values of  $q$ , lead us to respectively strong and weak specific interactions between the constituent components.

It is common practice to set  $k = 1$ ; and find a simplified Kwei equation as:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + q w_1 w_2 \quad (2)$$

For  $q = 0$ , eq. 1 reduces to the well-known Gordon-Taylor equation:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (3)$$

$k$  in the eq. 3, the same as  $q$  in eq. 2, is related to the strength of intermolecular interactions between the blend components.<sup>16-19</sup>

As shown in Figure 6, there is good agreement between the experimental data and calculated values

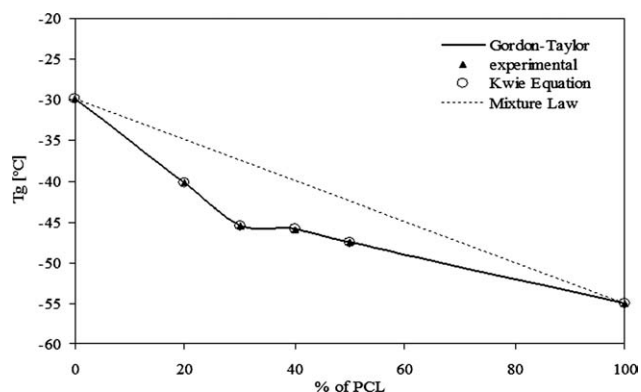


Figure 6 Composition dependency of glass transition temperatures ( $T_g$ ) for PU/PCL blends.



**TABLE 2**  
Values of  $q$  in Kwei and  $k$  in Gordon-Taylor Equations for PU/PCL Blends

Amount of PCL (%)	$q$	$k$
20	48.24	2.08
30	25.71	2.50
40	30.98	1.71
50	29.79	1.40

from the eqs. 2 and 3. The values of  $q$  in the eq. 2 and  $k$  in the Gordon–Taylor equation, are shown in Table II. The positive  $q$  and  $k$  values indicate a strong intermolecular interaction between PU and PCL.  $k$  and  $q$  values showed that increasing of the PCL content tends to decrease hydrogen bonding.

As seen in Figure 6, this blend system shows negative deviation from linear mixture law.

### Morphology of the PU/PCL blends

SEM micrographs of the fractured surface of PU/PCL blends with the compositions of 20, 30, 40, and 50 wt% of PCL are shown in Figure 7. The blend of 20 wt% is significantly homogeneous, called miscible blend, [Fig. 7(a)]. Miscibility depends on equal polarity or mutual attraction such as hydrogen bonding or cocrystallization.<sup>1</sup> So, as a result of FTIR spectra, miscibility of the blends decrease as a function

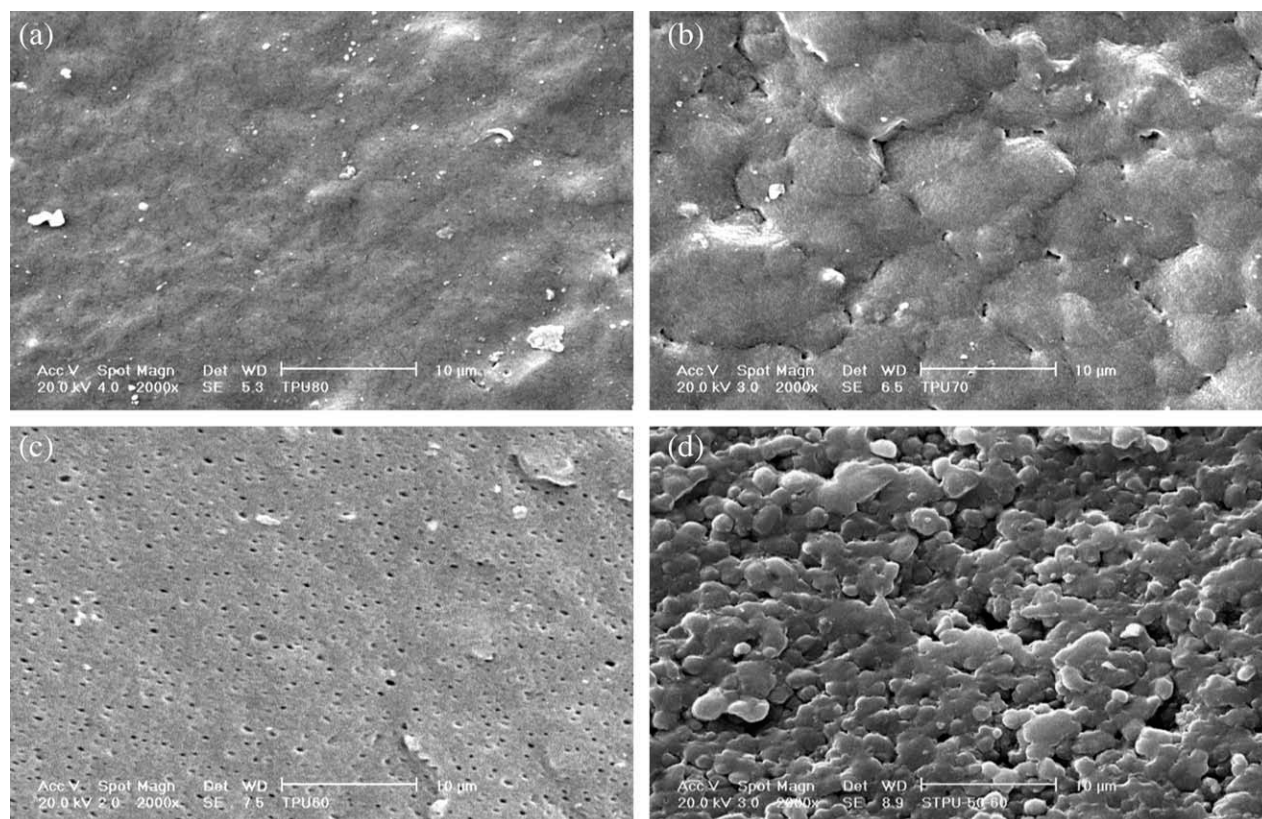
of increasing PCL content. SEM micrographs of PU/PCL blends, [Fig 7(a–d)], show some holes which attributed to the removed dispersed phase using the etching process with acetone. The increasing PCL content to 40 wt% [Fig. 7(c)], tends to increase the holes (or dispersed phase). Blend with 50 wt% of PCL shows co-continuous morphology [Fig. 7(d)]. Small domains in white color zone suggest the presence of microphase separation.<sup>20</sup>

### Rheological characteristics of PU/PCL blends

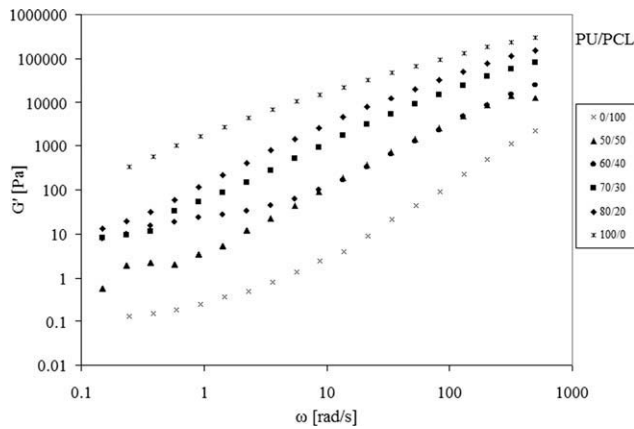
Figures 8–10 show the storage modulus,  $G'$ , loss modulus,  $G''$ , and complex viscosity,  $\eta^*$ , for net polymers and blends of 20, 30, 40, and 50 wt% of PCL. Because of adding a low moduli component, PCL, to high moduli PU, the increase of PCL in the blend causes the reduction of viscoelastic functions ( $G'$ ,  $G''$ , and  $\eta^*$ ).

The reduction of attractive hydrogen bonding in blends with adding PCL (according to FTIR and DSC results) could be mentioned as the other reason for downfallen of moduli and complex viscosity due to increasing the PCL content.

As seen, at high frequencies (Figs. 8–10),  $G'$ ,  $G''$ , and  $\eta^*$  values for PU/PCL (60/40) are quite similar to those of PU/PCL (50/50) blend. But at low



**Figure 7** SEM micrographs for (a) 80/20, (b) 70/30, (c) 60/40, and (d) 50/50 PU/PCL blends.



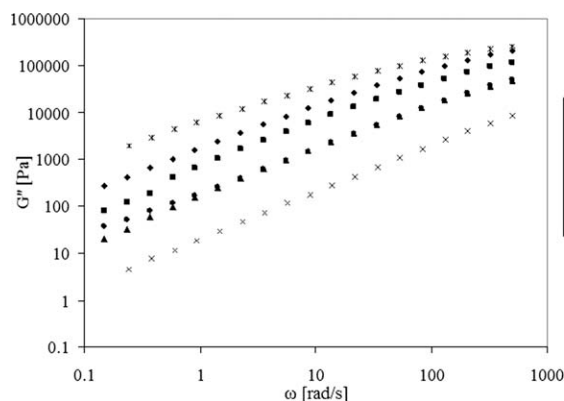
**Figure 8** Storage modulus of pure PU and PCL, and their blends at 200°C.

frequencies' region; these functions in 40 wt% of PCL are higher than those of 50 wt% of PCL.

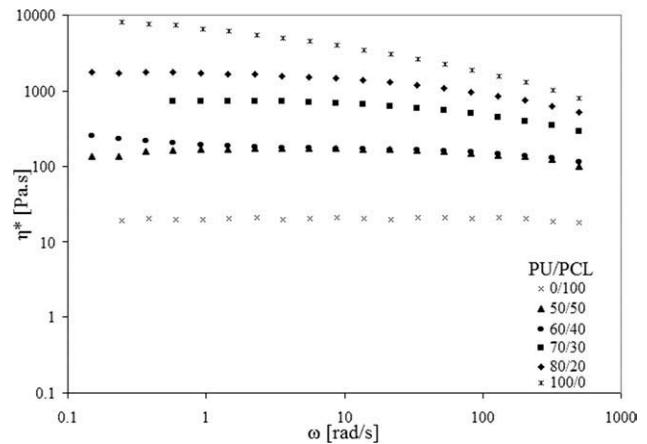
For many polymers, the slope of  $G'$  and  $G''$  at low frequencies is 2 and 1, respectively.<sup>6,18</sup> The polymer blends with specific interactions disobey from this rule. The slopes of  $G'$  and  $G''$  for PU/PCL blends are also much smaller than the above mentioned values, which imply to the existence of a significant amount of entanglement. Some of researchers suggested that the hydrogen bonds act as temporary entanglements and are in equilibrium between forming and breaking.<sup>21,22</sup>

In this investigation, the rheological data are limited to the range of 0.1–500 rad/s. we are interested in studying the rheological behavior of PU/PCL blend system at the broad frequency region from  $10^{-3}$  to  $10^4$  rad/sec. Therefore we calculated relaxation spectrum from the experimental data using UDS 200 software. The relaxation spectrum,  $H(\tau)$ , was determined by fitting the experimental  $G'(\omega)$  data, following a numerical differencing procedure developed.

From Figure 11, which displays  $H(\tau)$  versus relaxation time, we observe two peaks: the shortest relaxation time is related to PCL chains and the other one



**Figure 9** Loss modulus of pure PU and PCL, and their blends at 200°C.



**Figure 10** Complex viscosity of pure PU and PCL, and their blends at 200°C.

attributed to the hard segments of PU. With increasing PCL amount, the distance between the two peaks enhances. This can be related to decline the blend miscibility.

Subsequently,  $G'$  and  $G''$  are recalculated using the mentioned software based on eqs. 4 and 5. The result can be observed in Figure 12.

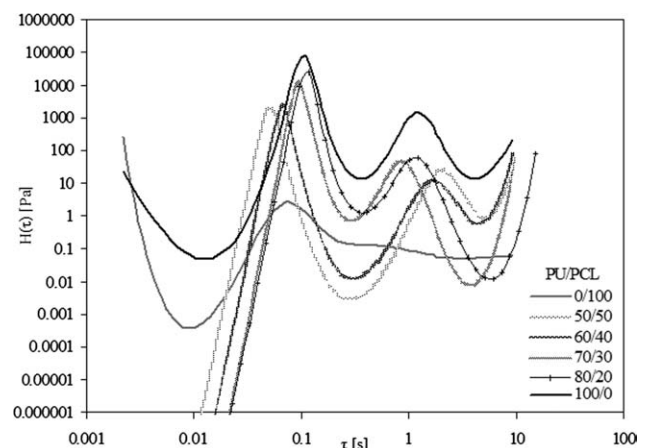
$$G' = \int_{-\infty}^{+\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} H(\tau) d(\ln(\tau)) \quad (4)$$

$$G'' = \int_{-\infty}^{+\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} H(\tau) d(\ln(\tau)) \quad (5)$$

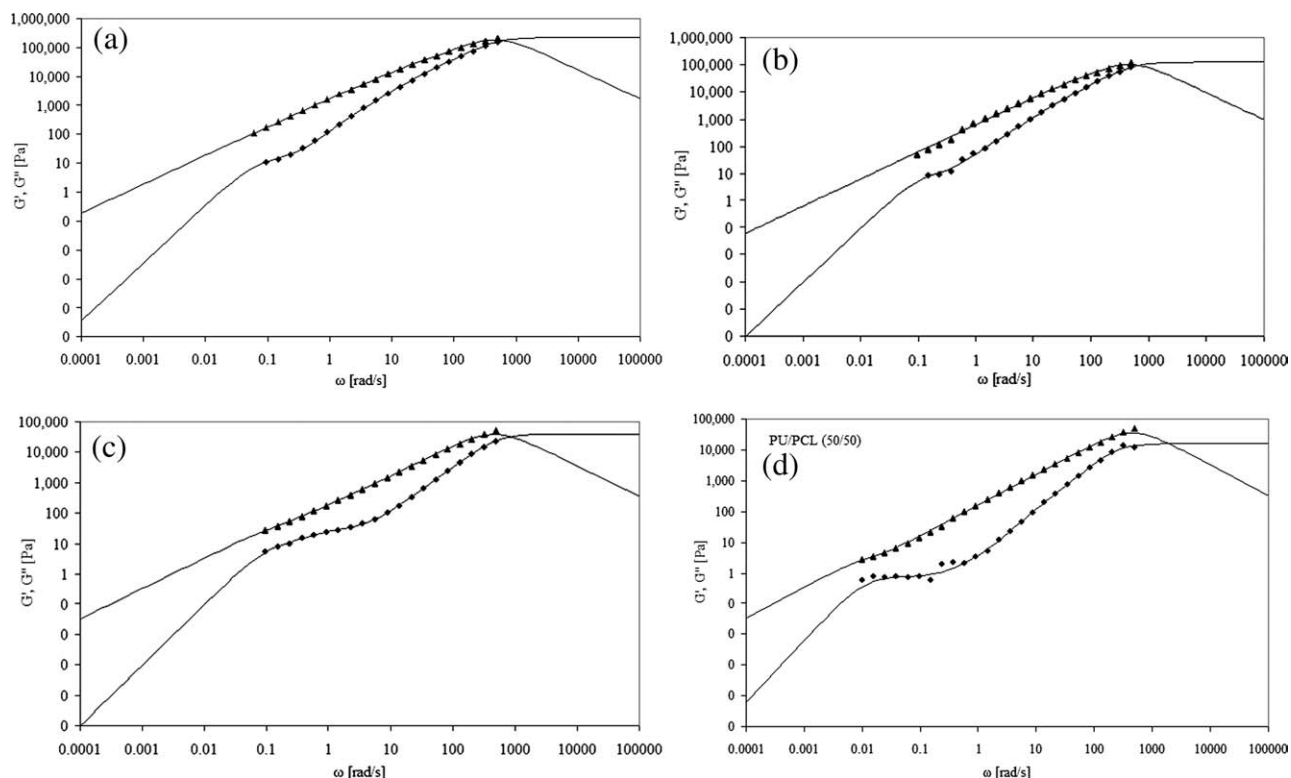
Now, we can calculate zero shear viscosity using the conventional method, eq. 6.

$$\lim_{\omega \rightarrow 0} \left( \frac{G''}{\omega} \right) = \lim_{\omega \rightarrow 0} \eta' = \eta_0 \quad (6)$$

Plateau modulus,  $G_N^0$ , can be estimated from the storage modulus at the frequency where a minimum of the loss tangent ( $\tan \delta$ ) occurs.<sup>24</sup>



**Figure 11** Relaxation spectrum for PU/PCL blends.

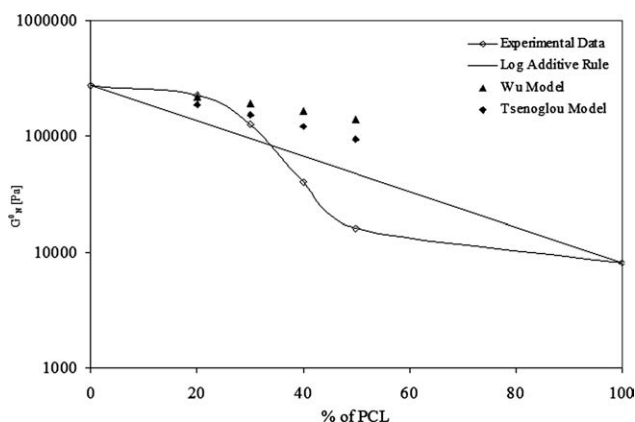


**Figure 12** Recalculated moduli obtained from relaxation spectrum for (a) 80/20, (b) 70/30, (c) 60/40, and (d) 50/50 PU/PCL blends.

Wu and Tsenoglou proposed two athermal equations (the eqs. 7 and 8, respectively) for describing the plateau modulus in miscible blends. They assumed that entanglement probability does not change by mixing. In these equations,  $\phi$  is volume fraction of components. Also, the subscripts 1, 2 and b indicate the dispersed, matrix and bulk phases, respectively.<sup>3</sup>

$$G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 \quad (7)$$

$$G_{Nb}^0 = (\phi_1 \sqrt{G_{N1}^0} + \phi_2 \sqrt{G_{N2}^0})^2 \quad (8)$$

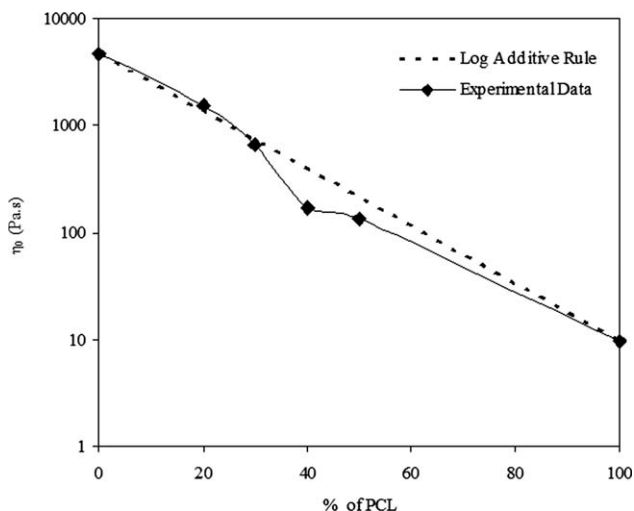


**Figure 13** Composition dependency of  $G_N^0$  for PU/PCL blends.

Figures 13 and 14 display  $G_N^0$  and  $\eta_0$  versus percent of PCL. As seen, these models could not predicted  $G_N^0$  values of our blends except of PU/PCL (80/20).

It is observed that the composition behavior of these functions at about 30 wt% converts from positive deviation of the log additive rule (eq. 9) to negative ones.

$$\log F_b = w_m \log F_m + w_d \log F_d \quad (9)$$



**Figure 14** Composition dependency of  $\eta_0$  for PU/PCL blends.

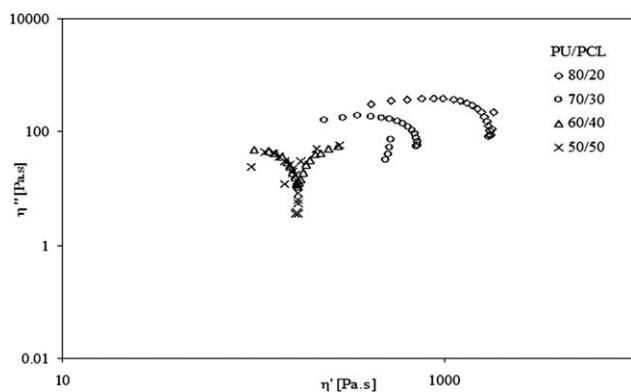


Figure 15  $\eta''$  versus  $\eta'$  for PU/PCL blends.

Where  $F$  is a viscoelastic function;  $w$  is the weight fraction; and the subscripts  $b$ ,  $m$ , and  $d$  indicate the values for blend, matrix, and dispersed phase, respectively.<sup>25</sup>

According to Figures 13 and 14, at low PCL contents,  $\eta_0$  and  $G_N^0$  exhibit low positive deviation from additive rule. Some researchers believed that miscible blends follow the log additive rule. The viscoelastic functions for immiscible blends, depending on the blend-composition, exhibit negative, positive and positive-negative deviation from the log additive rule. This trend were observed for plot of  $\eta^*$  and  $G'$  versus composition of PCL at low frequencies.<sup>26</sup>

Utracki has suggested two possible explanations for positive–negative deviations: partial miscibility at low concentration and concentration-dependent change of the flow mechanism in the immiscible region.<sup>27</sup> In blends with negative-positive (or reverse) deviation, some of investigators<sup>26</sup> suggested phase inversion occurred at the composition that the deviation changes from positive to negative (or reverse). In our work, this deviation can be attributed to the reduction of hydrogen bonding, while PCL content is increasing.

However, viscoelastic properties of the heterogeneous polymeric systems have a relaxation time dis-

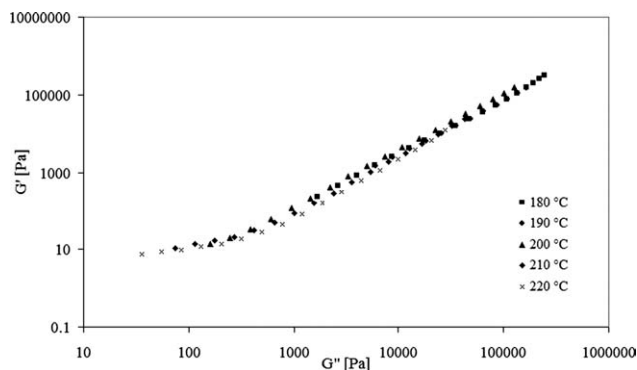


Figure 16  $G'$  versus  $G''$  for PU/PCL blends.

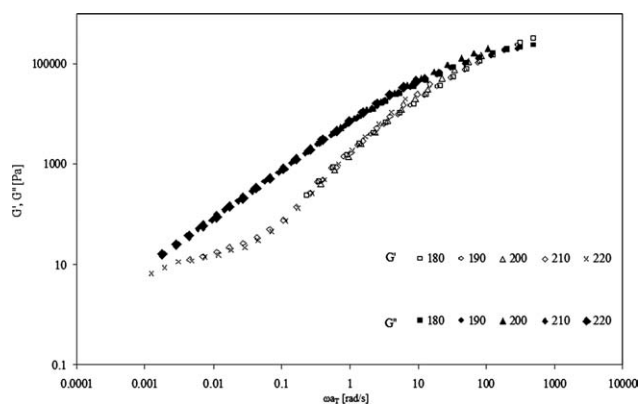


Figure 17  $G'$  and  $G''$  master curves for PU/PCL (80/20) blend at reference temperature of 180°C.

tribution described using the plots of the imaginary viscosity ( $\eta''$ ) versus the real one ( $\eta'$ ) (Cole–Cole plots). These plots for many polymer blends yield with two arcs, which were interpreted by the simultaneous occurrence of two processes with largely differing relaxation times. The homogeneous blends show only one circular arc in the curve, while for the immiscible blends, a tail or a second circular arc develops on the right-hand side of the arc which related to the formation of a second phase.<sup>28–32</sup>  $\eta''$ - $\eta'$  plots (Fig. 15) for this blend system display two different characteristic shapes. There is a tail on the right-hand side of the main arc, in 60/40 and 50/50 samples, while the 80/20 and 70/30 samples show a single arc. This behavior again confirms that morphology change occurs as the PCL content achieving around 20% of PCL, to a homogenous blend.

As mentioned in introduction, partially miscible polymer blends with homogenous structure follow TTS principle. In order to investigate TTS principle

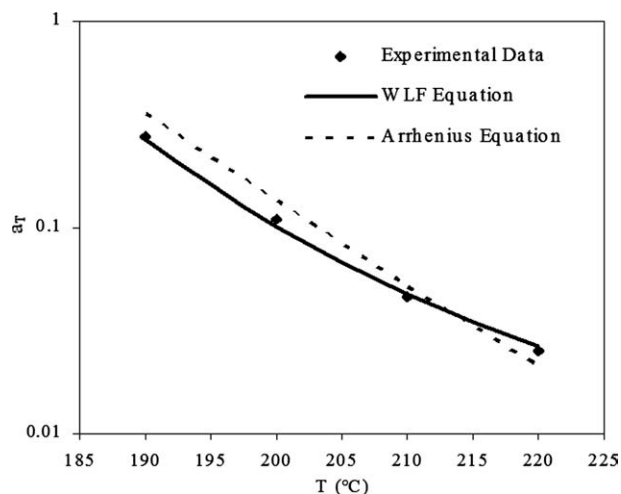


Figure 18 Temperature dependency of  $a_T$  for PU/PCL (80/20) blend.



in PU/PCL 80/20, frequency sweep tests were done on this blend at 5 temperatures, ie. 180, 190, 200, 210, and 220°C. Figure 16 show Cole-Cole plot of this blend system. The Cole-Cole diagram removes the effect of angular frequency. Therefore the effect of time or temperature disappears in this diagram. When TTS holds, the curve of  $G'$  versus  $G''$  is temperature independent, and a single curve is observed for all temperatures.<sup>28-32</sup> According to Figure 16, TTS is valid for PU/PCL (80/20) blend. Using horizontal shift factor,  $a_T$ , which reflects temperature dependence of the relaxation time, data of several temperatures superposed on values of 180°C and obtained master curve (Fig. 17).

Temperature dependency of  $a_T$  can be observed in Figure 18.  $a_T$  does not follow well-known Arrhenius pattern, which was assumed to be due to the presence of two different activation energies relating to the two phase separated domains of PU.<sup>33</sup> But WLF equation fitted the experimental values, well.

## CONCLUSIONS

In this article, thermal behavior and rheological properties of PU/PCL blends were investigated. FTIR results indicate the existence of hydrogen bonding in these blends which decreases with increasing of the PCL content. This tends to increase the microphase separation in the blends. SEM micrographs confirm these results. From DSC results using kwei and Gordon-Taylor equations, we also detect hydrogen bonding and partially miscibility of the blends. Rheological analysis pronounces the reduction of the viscoelastic functions with increasing the amount of PCL. The Cole-Cole plots and composition dependencies of these functions exhibit that the blend morphology changes above 30 wt% of PCL.

The slope of  $G'$  and  $G''$  were smaller than 2 and 1, respectively, because of the attractive hydrogen bonding between the constituents of blends. Existence of specific interactions causes validity of TTS principle for miscible PU/PCL (80/20) blend.

## References

- Harper, A. C. Handbook of Plastics Technologies: The Complete Guide to Properties and Performance; Technology seminars, Inc: Maryland, 2006.
- Lin, J. R.; Chen, L. W. J Appl Polym Sci 1998, 69, 1575.
- Ajili, S. H.; Golshan Ebrahimi, N.; Ansari, M. Rheol Acta 2008, 47, 81.
- Ajili, S. H.; Ebrahimi, N. G.; Soleimani, M. Acta Biomater 2009, 5, 1519.
- Li, R.; Yu, W.; Zhou, C. J Macromol Sci Phys 2007, 46, 1051.
- Yang, Z.; Han, C. D. Macromolecules 2008, 41, 2104.
- Shams Es-Haghi, S.; Yousefi, A. A.; Oromiehie, A. J Polym Sci Part B: Polym Phys 2007, 45, 2860.
- Pathak, J. A.; Colby, R. H.; Kamath, S. Y.; Kumar, S. K. Macromolecules 1998, 31, 8988.
- Pathak, J. A.; Gurp, M. V. J Appl Polym Sci 2000, 78, 1245.
- Jana, R. N.; Yoo, H. J.; Cho, J. W. Fiber Polym 2008, 9, 247.
- Wu, W.; Luo, X. L.; Ma, D. Z. Eur Polym J 1999, 35, 985.
- Yilgor, I.; Guler, I.; Ward, T.; Wilkes, G. Polymer 2006, 47, 4105.
- Lamba, N.; Woodhouse, K.; Cooper, S. The chemistry of polyurethane copolymers. In polyurethanes in biomedical applications; CRC Press: USA, 1998.
- Wang, L.; Wei, Y. Colloid Surf B 2005, 41, 249.
- Chun, Y. S.; Kyung, Y. J.; Jung, H. C.; Kim, W. N. Polymer 2000, 41, 8729.
- Nir, Y.; Narkis, M. Polym Eng Sci 1998, 38, 1890.
- Kuo, S. W.; Chang, F. C. Macromolecules 2001, 34, 5224.
- Yang, Z.; Han, C. D. Polymer 2008, 49, 5128.
- Meaurio, E.; Zuza, E.; Sarasua, J. R. Macromolecules 2005, 38, 1207.
- Sun, S.; Song, Y.; Zheng, Q. J Cereal Sci 2008, 48, 613.
- Park, H.; Hong, J. S.; Ahu, K. H.; Lee, S. J. Korea-Aust Rheol J 2005, 16, 79.
- Zhang, S.; Painter, P. C.; Runt, J. Macromolecules 2002, 35, 8478.
- Velázquez, O. D.; Hatzikiriakos, S. G.; Sentmanat, M. Rheol Acta 2008, 47, 19.
- Cai, H.; Ait-Kadi, A.; Brisson, J. Polymer 2003, 44, 1481.
- Nandan, B.; Khandpal, L. D.; Mathur, G. N. J Polym Sci Part B: Polym Phys 2004, 42, 1548.
- Mostafavi, F.; Ebrahimi, N. G. ISPST; Tehran: Iran, 2009.
- Utracki, L. A. Polymer Alloys and Blends: Thermodynamics and Rheology; Hanser: New York, 1989.
- Wu, D.; Zhang, Y.; Zhou, W. Eur Polym J 2008, 44, 2171.
- Yan, X.; Xu, X.; Zhu, T.; Zhang, C.; Song, N.; Zhu, L. Mater Sci Eng A 2008, 476, 120.
- Zheng, Q.; Du, M.; Yang, B.; Wu, G. Polymer 2001, 42, 5743.
- Ivonov, I.; Muke, S.; Kao, N.; Bhattacharya, S. N. Polymer 2001, 42, 9809.
- Perez, R.; Rojo, E.; Fernandez, M. Polymer 2005, 46, 8045.
- Krump, M. U. J Appl Polym Sci 2006, 100, 2303.