

# Rheological study of segmented polyurethane and polycaprolactone blends

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**Abstract** The dynamic rheological properties of segmented polyurethane based on polycaprolactone diol (PU-PCL *diol*) and poly ( $\epsilon$ -caprolactone) (PCL) blends were experimentally examined and theoretically analyzed using Palierne model. PU-PCL *diol* was melt blended with PCL in three different ratios of 20, 30, and 40%. Initial modeling attempts failed to fit the experimental data of these blends, as the model overpredicted their rheological data. This failure is believed to be due to partial dissolution of PCL in PU. According to our obtained results from differential scanning calorimetry and dynamic thermal mechanical analysis, pure PU-PCL *diol* is diluted by its homopolymer. By calculating the complex modulus of this diluted matrix using a simple mixing rule and its incorporation into the model, good fitting of the Palierne equation to the experimental data was obtained.

**Keywords** Rheology · Palierne model · Polyurethane · Poly ( $\epsilon$ -caprolactone) · Partial miscibility

## Introduction

Blending is one of the easiest ways to produce new materials with certain characteristics and specific applications. It is always interesting to determine blend characteristics based

on constituents properties and their composition. Many studies have been done up to date from both theoretical (Taylor 1932, 1934; Oldroyd 1953, 1955; Choi and Schowalter 1975; Palierne 1990; Doi and Ohta 1991; Almusallam et al. 2000; Bousmina et al. 2001; Lhuillier 2003) and experimental (Mani et al. 1992; Graebing et al. 1993; Kitade et al. 1994; Kapnistos et al. 1996; Guenther and Baird 1996; Lerdwijitjarud et al. 2003; Ansari et al. 2006) points of view, to predict the rheological behaviour of blends. According to these research works, blend behaviour merits special attention, because there are many differences between rheological properties of miscible and immiscible blends, due to the presence of an interface in immiscible systems as a third component with its own characteristics. Therefore, in studying such systems, the components' miscibility and blend structure must be taken into account.

To the best of our knowledge, apart from our previous works (Ajili et al. 2005, 2006), there is no rheological study on segmented polyurethane (PU) and poly ( $\epsilon$ -caprolactone) (PCL) blends in which PU contains blocks chemically identical to PCL. In our previous work (Ajili et al. 2005), the micromechanical Coran model was employed to predict dynamic rheological behaviour of PU/PCL blends. The results showed that Coran model fitted the experimental data, but the values of  $f$  (fitting parameter), which give a measure for the continuity of the phase with the highest modulus (PU in comparison with PCL), were low. This was not, however, in agreement with morphological observations. The reason for this observation, which may be related to microstructure of each constituent, motivated us to do a detailed study about rheological behavior of this blend system by Palierne model and its relationship with components' miscibility or blend behaviour. Thermo-physical measurements such as dynamic mechanical thermal analysis and differential scanning calorimetry (DSC) used to study about blend behaviour.

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## Experimental

### Materials

Polyester-urethane based on polycaprolactone-diol (as a soft segment [SS] with  $M_n$  of 2,000 g/mol) is a commercial food grade PU (LPR2102-85 AE) which was delivered from Coim (Italy) with a density of 1.16 g/cm<sup>3</sup>. PCL was obtained from Sigma-Aldrich (Germany) with  $M_n$  of 42,500 g/mol, density of 1.145 g/cm<sup>3</sup>, and melting point of 60 °C.

### Blends preparation

Three different blends of PU–PCL diol and PCL with PCL contents of 20, 30, and 40 wt% were prepared, which are labeled through this paper as PU/PCL-20, PU/PCL-30, and PU/PCL-40, respectively. All these blends were prepared by melt mixing in a Brabender internal mixer at 200 °C and a rotor speed of 50 rpm for approximately 5 min (time to attain a constant torque). The procedure is as following: First of all, TPU–PCL diol was fed into the preheated mixer to be melted, and then, PCL was introduced into it.

It should be mentioned that TPU–PCL diol was dried for at least 1 h in a 100 °C vacuum oven before melt blending to prevent any bubble formation in the samples.

### Morphological characterization

The morphology of the blends 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. The morphology was quantified using an appropriate software (KS 300). The average diameter of the minor phase was calculated after analysis of the SEM micrographs. About 20 particles were considered to calculate this parameter.

### 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).

### Differential scanning calorimetry

The melting and crystallization behaviour of the polymer blends were studied by a Mettler differential scanning

calorimeter (model Star SW 8.01) in a dry nitrogen atmosphere. The sample was cooled to –90 °C from the melt of the first scan at a cooling rate of –20 °C/min scanned between –90 and 210 °C at 10 °C/min, and  $T_m$  was determined. The crystallization temperature ( $T_c$ ) was found by cooling the samples from 80 °C at a cooling rate of –10 °C/min.

### Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out at 1 Hz and 2 °C/min heating rate by using dynamic mechanical analyzer (DMA 242, Netzsch). The tests were performed on strip specimens with dimensions of 10×4×0.1 mm<sup>3</sup> at tension mode.

### FTIR characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad FTS-40A operated with a dry air purge. Samples were prepared as films by compression molding and vacuum drying for 1 day at 60 °C (50 °C for PCL).

## Results and discussion

### Theory

Palierne (1990) has developed a theoretical model for complex modulus of blends based on complex modulus of each phase, the hydrodynamic interactions, the droplet size and size distribution, and the interfacial tension. In this model, it was assumed that the droplets maintain their spherical shapes during the flow, and thus, it is only applicable in linear viscoelastic regime. Equations 1a and 1b are the simple form of main Palierne model in which droplets size distribution and the terms for describing dilatation modulus and shear modulus of the droplets surface have been ignored (Shi et al. 2002).

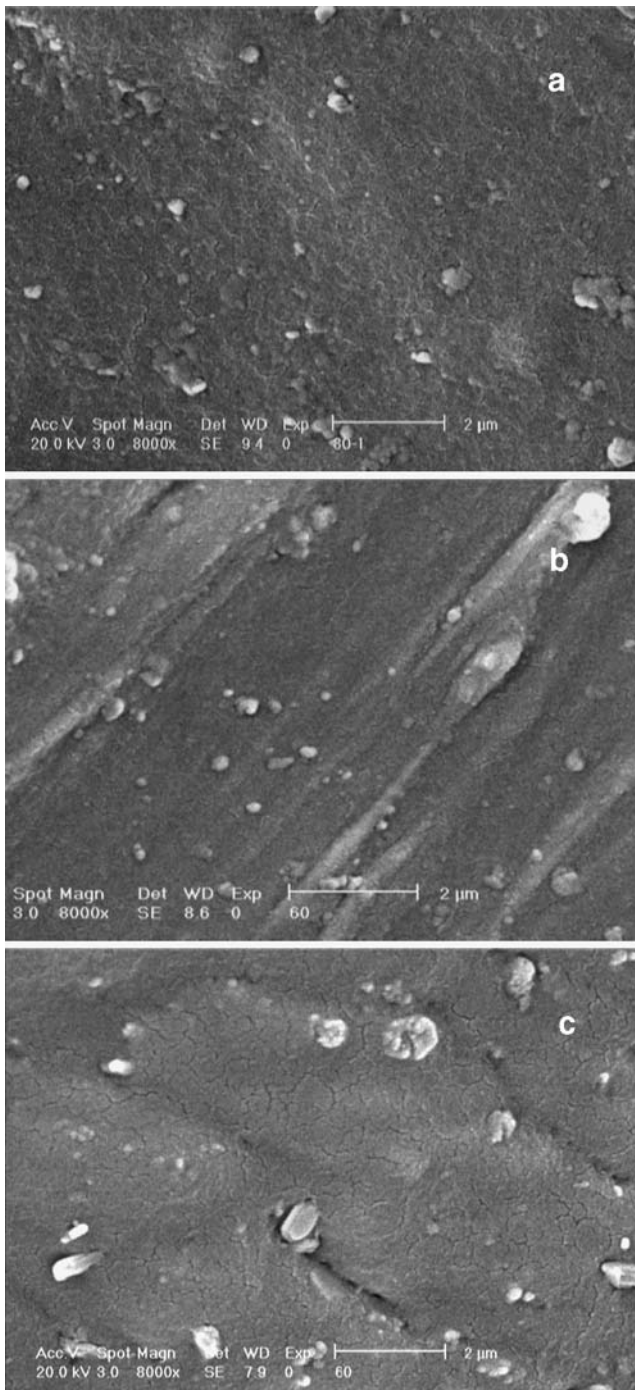
$$G_b^*(\omega) = G_m^*(\omega) \frac{1 + 3\phi H(\omega)}{1 - 2\phi H(\omega)} \quad (1 - a)$$

$$H = \frac{4(\alpha/R) [2G_m^* + 5G_d^*] + [G_d^* - G_m^*] [16G_m^* + 19G_d^*]}{40(\alpha/R) [G_m^* + G_d^*] + [2G_d^* + 3G_m^*] [16G_m^* + 19G_d^*]} \quad (1 - b)$$

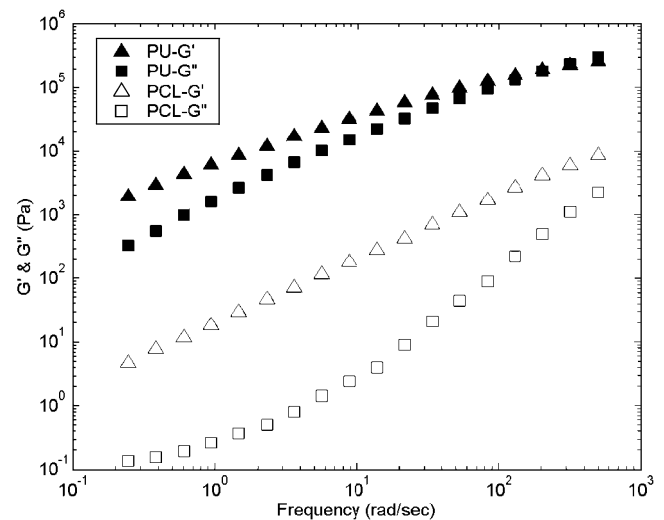
In this equation,  $\phi$ ,  $\alpha$ ,  $R$ ,  $G_b^*$ ,  $G_d^*$ , and  $G_m^*$  are volume fraction, interfacial tension, radius of dispersed droplets, and complex moduli of blend, dispersed phase, and matrix, respectively.

## Results

SEM micrographs of the fractured surfaces of the binary blends are shown in Fig. 1a–c. A droplet dispersion morphology type can be observed. From Fig. 1, it can be seen that the size of the dispersed phase increases as a function of increasing PCL content. It seems that interfacial adhesion of two phases is reduced with PCL content, which is discussed later.



**Fig. 1** Morphology of PU/PCL blends: **a** 80/20, **b** 70/30 and **c** 60/40



**Fig. 2** Storage and loss moduli of PU and PCL at 200 °C

Figure 2 shows the storage and loss moduli of the pure polymers, respectively. A large difference between dynamic moduli of both components is observed.

In Figure 3a–b, the storage and loss moduli of PU/PCL-20, PU/PCL-30, and PU/PCL-40 blends are shown. Attempts to fit the data with Palierne model failed, and error was minimized with negative  $\alpha/R$  as fitting parameter, which is unrealistic physically. It must be noted that the solid lines in Fig. 3a–b are model predictions with  $\alpha/R=0$ . This may be attributed to partial dissolution of PCL in PU together with a large difference between moduli of dispersed (PCL) and matrix (PU) phases (the case was reported for high-density polyethylene and nylon 66 blends by Kim and Seo 2003). These reasons led to a large decrease in the matrix phase modulus, and therefore, as it is shown in Fig. 3, overpredictions of the experimental data are observed.

As mentioned before, because of microstructural similarity of PCL with the SS of PU, it is believed that some parts of PCL are dissolved in the PU to form a “new matrix” of lower modulus than pure PU. Because the PCL used has a higher molecular weight than PCL blocks in PU and chains with higher molecular weight generally 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 semimiscible or “partially miscible” (Bonner and Hope 1993). The schematic of this blend structure is shown in Fig. 4.

To check the semimiscibility of this blend system, a couple of thermal tests has been performed, i.e., DMA and DSC (Chun et al. 2000).

Figure 5 shows the DSC thermograms of pure PCL and various TPU–PCL diol/PCL blends at a cooling rate of  $-10$  °C/min from 80 °C. As depicted in Fig. 5,  $T_c$  of the

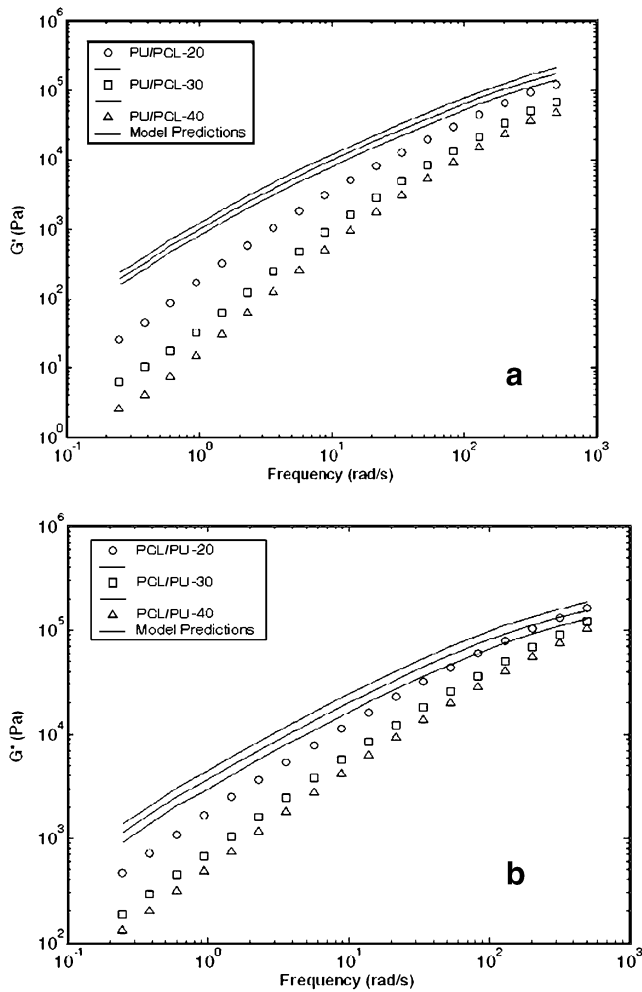


Fig. 3 Storage (a) and loss (b) moduli of PU/PCL-20, PU/PCL-30, and PU/PCL-40 and Palieme model prediction with  $\alpha/R=0$

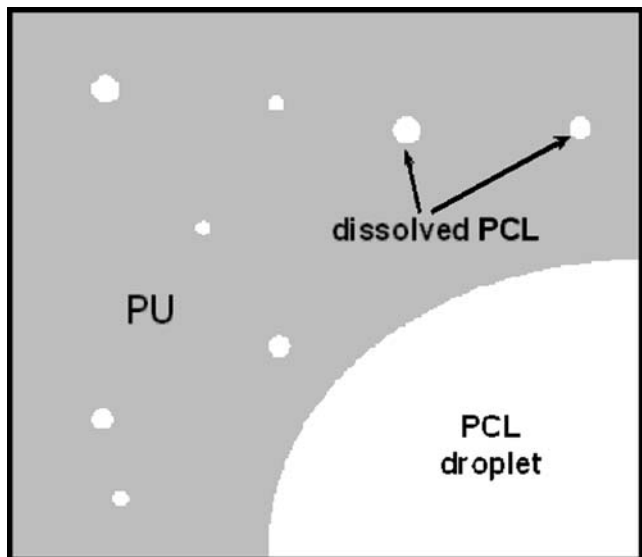


Fig. 4 Schematic of partially miscible PU/PCL blend

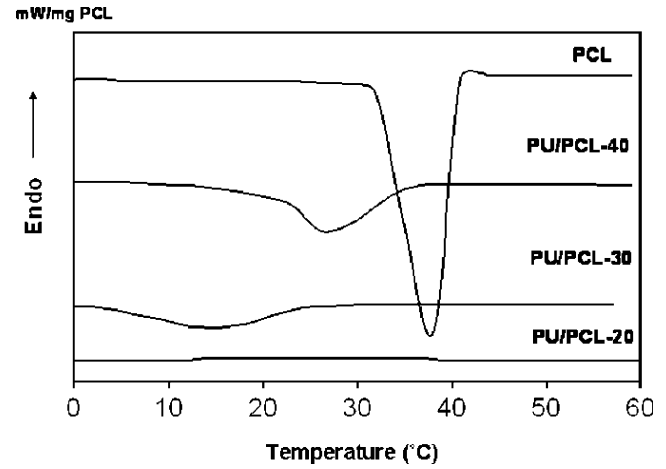


Fig. 5 DSC scans of TPU–PCL diol/PCL blends with different compositions at a cooling rate of  $-10\text{ °C/min}$  from  $80\text{ °C}$

PCL component in the blend decreases significantly with an increase of TPU–PCL diol content in comparison with pure PCL and becomes less sharp. This suppression of  $T_c$  indicates that TPU–PCL diol may slow down or even inhibit the PCL crystallization in the blends (Kuo et al. 2004).

Furthermore, Fig. 6 shows the DSC heating thermograms of pure PCL and various TPU–PCL diol/PCL blends after cooling the samples under the same conditions.  $T_m$  of the PCL component in the blend decreases with an increase in the TPU–PCL diol content. Depression of both crystallization temperature and melting point are indications of compatibilization taking place in these blends (Ajili and Ebrahimi 2006).

The DMA results for TPU–PCL diol, PCL, and their blends are displayed in Fig. 7. According to these results, the two  $T_g$ 's (peak positions in  $E''-T$  graphs) observed one for each component in the blend, change their positions relative to that of the pure polymer, approaching each other.

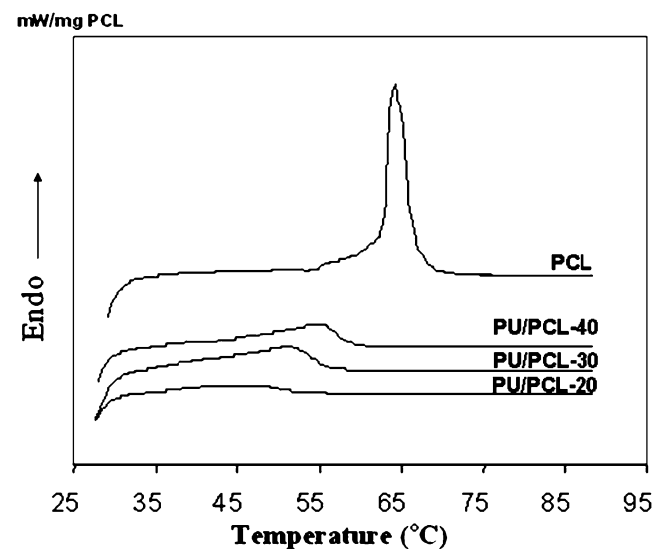


Fig. 6 DSC scans of TPU–PCL diol/PCL blends with different compositions at a heating rate of  $10\text{ °C/min}$  from  $30\text{ °C}$

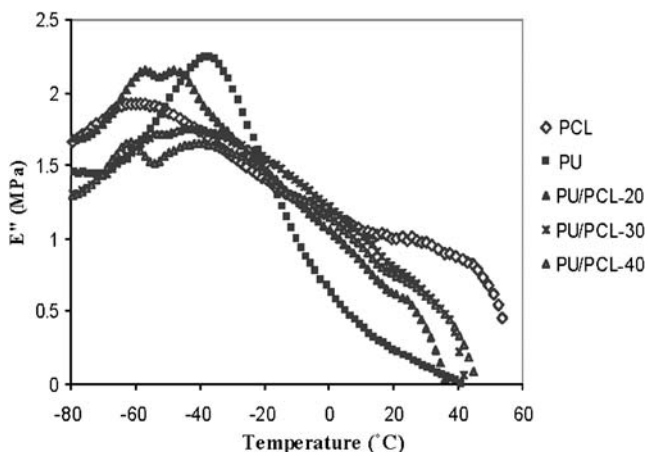


Fig. 7 Dynamic mechanical spectra for TPU–PCL diol/PCL blends

This means that the blends are partially miscible (Scobbo 2000).

Therefore, the matrix in PU/PCL blends is not pure PU. To calculate the modulus of this “new matrix” (PU+ dissolved PCL), which is a miscible system, an appropriate mixing rule is required. Wu (1987) and Tsenoglou (1988) proposed two athermal equations (Eqs. 2 and 3, respectively) for describing the plateau of modulus for miscible blends in which it is assumed that entanglement probability does not change by mixing. In these equations,  $G_N^0$  is modulus value, and  $\phi$  is blend composition. Subscripts 1, 2, and b indicate the dispersed, matrix and bulk phases, respectively.

$$G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 \tag{2}$$

$$G_{Nb}^0 = \left( \phi_1 \sqrt{G_{N1}^0} + \phi_2 \sqrt{G_{N2}^0} \right)^2 \tag{3}$$

However, Cai et al. (2003) checked these *mixing rules* for blends of PVPh/PEO representing a miscible system with hydrogen bonding interactions between the component chains and found that both of these equations overpredict experimental data, although they hold true for miscible blends without any strong interaction; this is even true for the Tsenoglou equation (Lomellini 1992). With a careful insight into their experimental data, it is found that Eq. 4 is in good agreement with their results, and hence, with notion that our blends also have hydrogen bonds (between amide groups of PU and carbonyl groups of PCL), we preferred to use Eq. 5 as a “mixing rule” to calculate matrix modulus ( $G_m^*$ ), where  $\phi'$  is volume fraction of PCL dissolved in PU.

$$1/G_{Nb}^0 = \phi_1/G_{N1}^0 + \phi_2/G_{N2}^0 \tag{4}$$

$$1/G_m^* = (1 - \phi')/G_{PU}^* + \phi'/G_{PCL}^* \tag{5}$$

Considering partial miscibility of the blend system, we employed Palierne model (Eq. 1) again to predict the rheological data using  $G_m^*$  term from the Eq. 5. It must be noted that  $\phi$  in Eq. 1 is the volume fraction of PCL droplets in the matrix (see Fig. 4). Two parameters of  $\alpha/R$  and  $\phi'$  were optimized for the best fit of the experimental data. With this assumption, fittings were obtained well. The results are shown in Fig. 8a and b. As we can see from Fig. 8, there are slight discrepancies between model prediction and experimental data for PU/PCL-40 blend. This is due to the fact that, in Palierne model, steric interactions and anisotropic effects, which often occur in concentrated systems, are not included and these shortcomings limit the applicability of this model from a low up to a moderate volume fraction of dispersed phase where there is no coalescence (Jafari et al. 2005).

The mean radius of dispersed phase according to SEM observation and the  $\alpha$  value corresponding to the best fit,

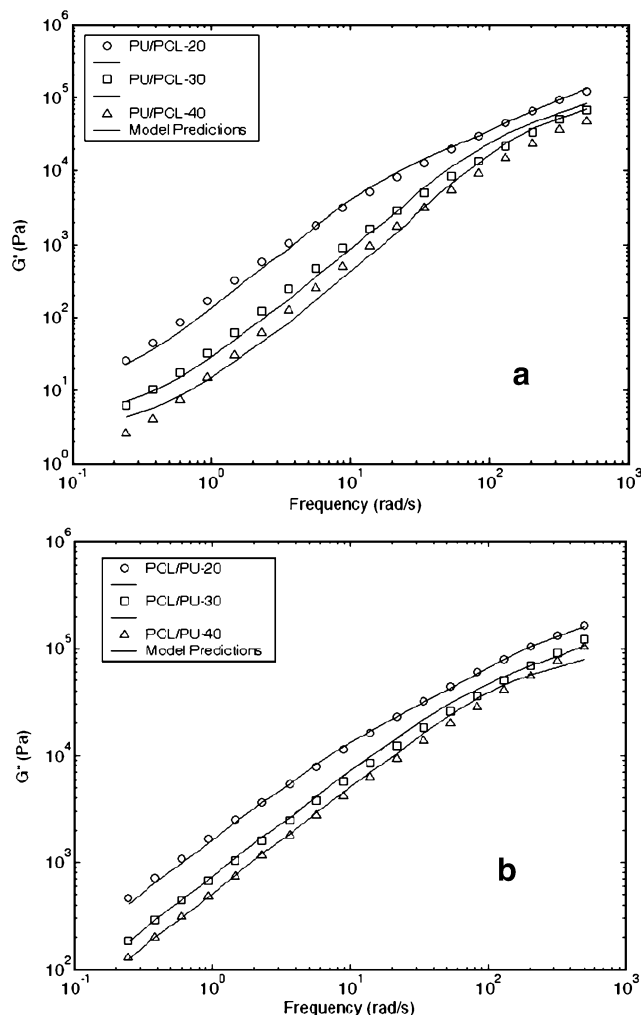


Fig. 8 Storage (a) and loss (b) moduli of PU/PCL-20, PU/PCL-30 and PU/PCL-40 and Palierne model prediction with dissolution assumption

**Table 1** Blend parameters obtained from second fitting and SEM observations

Blend	$\phi'$ (%)	$\alpha/R$ (Pa)	$R$ ( $\mu\text{m}$ )	$\alpha$ (mN/m)
PU/PCL-20	1.18	4.27e+4	0.33	14.09
PU/PCL-30	3.24	9.90e+4	0.36	35.64
PU/PCL-40	5.38	12.04e+4	0.49	58.99

for the blends, are given in Table 1. Results show that the  $\alpha$  depends on the composition of the blends.

It is suggested that this difference is caused by the change of PU microphase structure in the blends. Segmented PUs contain two phases, which are the flexible SS and the rigid hard segment (HS). It is generally believed that one of the most important factors or driving forces for the microphase separation of both phases in PUs is the strong hydrogen bonding between the urethane HS. Analysis of the difference in intensity of  $N-H$  peak in FTIR spectra provides valuable information in understanding the extent of microphase separation (and or phase mixing) in PUs (Yilgor et al. 2006). The FTIR spectra in the region of 1,550–3,200  $\text{cm}^{-1}$  for PU, PCL, and their blends are given in Fig. 9. In these spectra, the peak at 3,115  $\text{cm}^{-1}$  may be assigned as a peak related to bending vibration of  $N-H$  group in HS. There is another absorption peak at 1,600  $\text{cm}^{-1}$ , which is due to stretching vibration of  $C=C$  in benzene ring of urethane (Lamba et al. 1998).

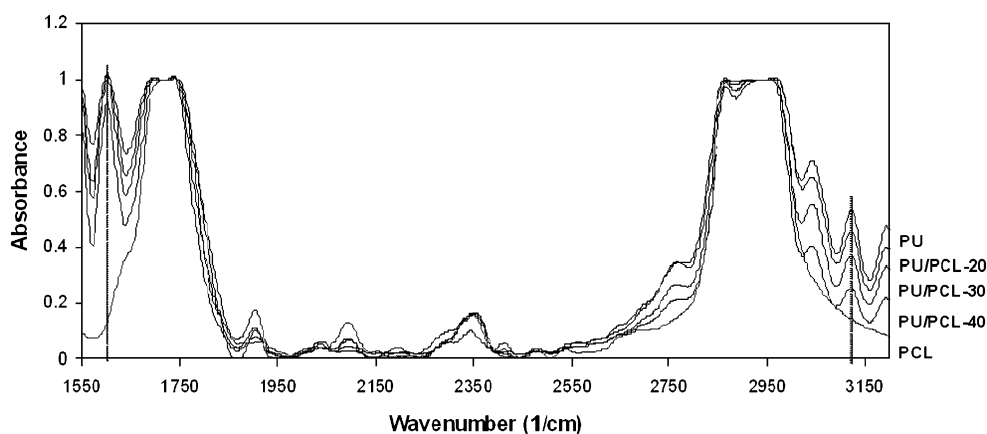
In Table 2, the intensity ratio of  $N-H$  bending peak over  $C=C$  stretching peak for pure PU and their blends is given. We used this relative intensity to correct the effects of concentration and thickness differences in the samples. From Table 2, it is found that the relative intensity of  $N-H$  bending peak in the blends decreases with increasing the PCL content. This decrease indicates that the bending vibration of  $N-H$  groups in urethane HS has been restricted in the blends because of increasing fraction of HS–HS hydrogen bonding. Therefore, we can say that the morphology of PU in the blends shifts from phase mixing with a non- or loosely hydrogen-bonded interactions toward

**Table 2** The relative intensity of absorbance at 3,115  $\text{cm}^{-1}$ (a) to that one at 1,600  $\text{cm}^{-1}$  (b)

Sample	$a/b$
PU	0.57
PU/PCL-20	0.43
PU/PCL-30	0.37
PU/PCL-40	0.21

phase separation with strongly hydrogen-bonded ones as PCL content is increased. This is due to incorporation (dissolution) of PCL into PU SS, which are miscible. On the other hand, miscibility of PCL and SS of PU increases the amount of phase separation between HS and SS of PU in the blends that are thermodynamically immiscible. This behaviour was also reported for miscible PVC/PU blends by Wang and Cooper (1981). The change of PU morphology in the blends leads to a change in the nature of interfacial region between the matrix and dispersed phases. Another research (Wang and Wei 2005) has demonstrated that the ratio of  $N/C$  groups at surface and bulk region of PU is reduced, when the amount of phase separation is increased. Hence, we can say that  $N(-H)/C$  ratio is decreased at interfacial region of PU/PCL blends along with degree of urethane separation. As the amount of phase separation depends on the extent of PCL dissolved in PU ( $\phi'$ ) and it is varied in the blends, thus their interfacial tension are not the same.

The difference in interfacial tension is quantitatively detectable from morphological observation. In high concentration of PCL (PU/PCL-40 blend), the poor interfacial adhesion due to poor interaction is evident from the size of dispersed phase and weak interface, but in the blends with lower content of PCL, PU molecules have more effective functional group ( $N-H$ ) acting at the interface to reduce the  $\alpha$  value. These observations support the increase trend of interfacial tension of two phases, which was obtained from fitting of the model to the experimental data.

**Fig. 9** FTIR spectra of PU, PCL and PU/PCL blends in the region of 1,550–3,200  $\text{cm}^{-1}$ 

## Conclusions

Linear viscoelastic properties of PCL, PU, and their blends have been studied in frequency sweep experiment. It was observed that Palierne model could not fit the rheological data at all. This was attributed to partial miscibility of the blends. In these blends, partial dissolution of PCL in PU along with the large difference between the dynamic moduli of PU (matrix phase) and PCL (dispersed phase) led to a large reduction in matrix modulus. By taking into account the partial miscibility of the blends, confirmed by DSC and DMTA results, Palierne model fitted the data well. Utilizing drop size information collected by SEM observations, estimates for composition-dependent interfacial tension were also produced. The present research also shows that, the low value of  $f$  (fitting parameter in Coran model) for these blends is attributed to a low continuity of PU as a bulk phase due to partial miscibility of this blend system.

In this study, it is concluded that, with the aid of rheological analysis, it is possible to characterize the blend structure and miscibility of constituents qualitatively.

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