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Interactions in polymer blends based on polyesterurethanes investigated by thermal analysis

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Abstract

TPU and chlorinated thermoplastic polyurethane (CTPU) were synthesized by using a two-step solution polymerization technique from poly(caprolactone) (CAPA), 4′,4-diphenyl-methanediisocyanate (MDI) and 1,2-propandiol (PD) or 3-chloro-1,2-propandiol (CPD) for CTPU, respectively.

TPU and CTPU were blended with styrene/acrylonitriles (SANs) with a different amount of acrylonitrile within the entire compositional range. The blends were prepared as films from 15 wt% solution in dimethylformamide (DMF).

The thermal properties of TPU, CTPU, SANs and their blends, as well as the influence of the amount of acrylonitrile (AN) component in SANs on the thermal behavior of blends, were studied by differential scanning calorimetry (DSC). The Flory–Huggins interaction parameter (χ_{12}) was estimated.

Keywords: Interactions; Polyesterurethanes; Polymer blends; Thermal analysis

1. Introduction

Various physical properties of polymer blends are particularly interesting because they depend on the composition, phase structure, and interactions between components, as well as on the conditions of preparation. Casting from solution in a common solvent is a widely used method for preparation of blends.

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Thermoplastic polyurethanes (TPUs) are materials with a wide range of chemical and physical properties [1]. The immiscibility and interactions of soft and hard segments of TPUs cause a characteristic microphase structure. Because of this, the structure of polymer blends of thermoplastic polyurethane with other plastomers is very complex.

The thermal and mechanical properties of TPUs synthesized under different polymerization process conditions have been studied by many authors [2,3]. Ho and Wynne [4] and Yoon et al. [5] investigated the properties of TPU with a halogenated chain extender.

Thermal properties of blends of TPU with chlorinated thermoplastic elastomers [6, 7, 8] have been reported and TPU blends with styrene/acrylonitrile (SAN) [9, 10, 11] have also been investigated.

Two polymers are mutually miscible only if their free energy of mixing is negative [12, 13]. In most cases, the mixing of polymers is endothermic; the miscibility of high molar mass polymers is an exception. Miscibility is improved if there are some interactions in the system.

Thermodynamics is the key to understanding the behavior and properties of blends and also defines the possibilities of their commercial applications. In polymer blends, the configurational entropy is small and the free energy of mixing can be expressed as [12,13,14,15]

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

where ΔH_m and ΔS_m are the enthalpy and the entropy of mixing, respectively.

Flory–Huggins theory makes it possible to calculate the interaction parameter (χ_{12}). Scott and Tompa were the first to apply the theory of solutions to polymer blends with the purpose of determining the χ_{12} [12]

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12}\phi_1\phi_2(m_1 n_1 + m_2 n_2) \tag{2}$$

where n_i is the number of moles of the ith component in the blend and $m_i = M_{n,i}/\rho_i$ (ρ_i is the density of the ith polymer, $M_{n,i}$ is the average molar mass of the ith polymer). The volume fraction of the ith component is $\phi_i = m_i n_i/(m_i n_i + m_j n_j)$ ($i, j = 1$, 2 and $i \neq j$).

If the required equilibrium conditions are met, then Eqs. (3) and (4) could be used as a final expression for calculating the χ_{12} in the partially miscible or immiscible blends [14]

$$\chi_{12} = \frac{\ln\dfrac{\phi_1''}{\phi_1'} + \left(1 - \dfrac{m_1}{m_2}\right)(\phi_2'' - \phi_2')}{m_1(\phi_2'^2 - \phi_2''^2)} \tag{3}$$

$$\chi_{12} = \frac{\ln\dfrac{\phi_2''}{\phi_2'} + \left(1 - \dfrac{m_2}{m_1}\right)(\phi_1' - \phi_1'')}{m_2(\phi_1'^2 - \phi_1''^2)} \tag{4}$$

where ϕ_i' is the volume fraction of the ith component in the ith-component-rich phase and ϕ_i'' is the volume fraction of the ith component in the ith-component-poor phase. Subscripts 1 and 2 denote polymers, $\phi_1' + \phi_1'' = 1$ and $\phi_2' + \phi_2'' = 1$, respectively.

The χ_{12} calculated according to Eqs. (3) and (4) gives different values, which should be averaged to minimize error in the calculated χ_{12}. A simple thermodynamic model for polymer–polymer blends based on the theory of Flory–Huggins leads to the important conclusion that the miscibility in the limit of higher molar mass requires a negative χ_{12}.

In the present work, TPUs based on poly(caprolactone) (CAPA) and 4′,4-diphenylmethanediisocyanate (MDI) extended with 1,2-propanediol (PD) or 3-chloro-1,2-propanediol (CPD) were synthesized and then blended with SANs with different amounts of acrylonitrile (AN) component.

The thermal properties of blends of TPU and chlorinated thermoplastic polyurethane (CTPU) with SANs were investigated by differential scanning calorimetry (DSC). The χ_{12} values were estimated on the basis of the averaged molar mass and densities obtained.

2. Experimental

2.1. Materials

TPU and CTPU were synthesized from CAPA ($M_n = 2000$, Interox), MDI (Bayer) and PD or CPD (Merck), in solution by the standard prepolymer process.

The prepolymer synthesis was carried out at 343 K for 6 h. The viscosity of the reaction mixture was adjusted to approximately 50 wt% by dimethylformamide (DMF). The final ratio of NCO:OH was 1:1. The extent of the reaction in the prepolymer step was determined by titration of the unreacted –NCO groups (ASTM D 1638-74). The course of the second step of the reaction was followed by the attenuation of the intensity of the isocyanate stretching band at 2270 cm^{-1} relative to the intensity of the C–H band at 2940 cm^{-1}.

Commercial SAN1 (Luran 388 S, BASF) with 32.9 wt% of acrylonitrile and SAN2 (Luran 368 R, BASF) with 23.9 wt% of acrylonitrile were applied for blending with TPU and CTPU. The average molar masses (M_n) of all the polymers used were determined by gel permeation chromatography (GPC) (Perkin-Elmer), relative to the polystyrene standard. The values were 88600 for TPU, 92000 for CTPU, 188000 for SAN1 and 192000 for SAN2.

2.2. Blends preparation

TPU or CTPU and SANs were dissolved in dimethylformamide (DMF) in ratios of 100:0, 90:10, 75:25, 60:40, 50:50, 40:60, 25:75, 10:90, 0:100 at room temperature. Films with a thickness of 300 μm were cast from the solution (15 wt%) and dried in a vacuum at 313 K for 6 h. The thickness of the dry films was approximately 30 μm.

2.3. DSC measurements

The thermal properties of the pure polymers and blends were measured using a Perkin-Elmer differential scanning calorimeter (DSC-7). The samples were heated at a rate of 20 K min^{-1} in the ranges :

203–298 K: to determine the glass transition temperatures of soft segments ($T_{g,\mathrm{soft}}$) of TPU and CTPU;

298–503 K: to determine the glass transition temperatures of TPU and CTPU of hard segments ($T_{g,\mathrm{hard}}$), the glass transition temperatures of SAN ($T_{g,\mathrm{SAN}}$), and also the melting temperatures of soft segments of TPU and CTPU (T_m).

3. Results and discussion

3.1. Thermal properties of TPU and CTPU and their blends with SANs

The glass transition temperature of the soft segments ($T_{g,\mathrm{soft}}$) of pure TPU and CTPU, i.e. polycaprolactone, was found to be approximately 242 K (Fig. 1). Curves indicate that the addition of SAN1 (up to 25 wt%) does not have a great influence on the structure of the soft segment in TPU and CTPU. The changes in the structure of the

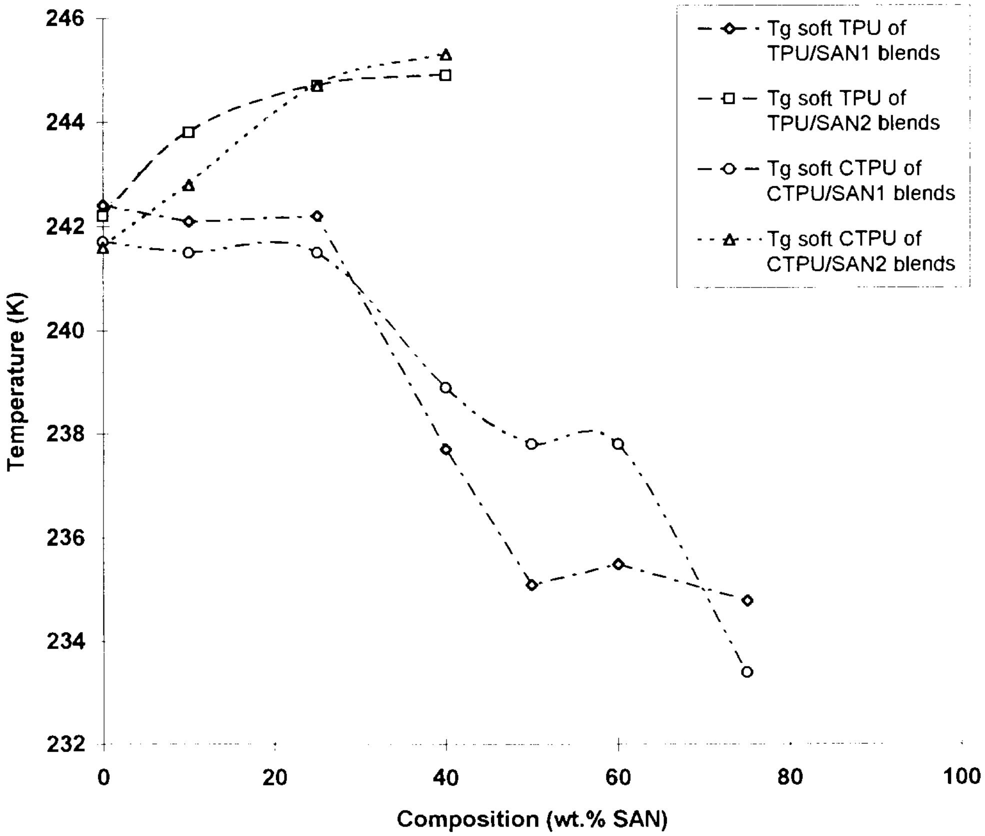

Fig. 1. $T_{g,\mathrm{soft}}$ of TPU and CTPU in their blends with SAN1 and SAN2.

soft segment of TPU and CTPU, expressed by $T_{g,\mathrm{soft}}$ values, are noticed when TPU and SAN1 or CTPU and SAN1 have approximately the same concentration. The addition of SAN2 to TPU and CTPU causes a slight increase of the $T_{g,\mathrm{soft}}$ values. The blends have the same $T_{g,\mathrm{soft}}$ values at 25 wt% addition of SAN2 to TPU and CTPU. In the DSC curves, the $T_{g,\mathrm{soft}}$ values were seen to go up to 75 wt% for the blends of TPU and CTPU with SAN1 and only up to 40 wt% for the blends with SAN2.

Melting peaks (T_m) of pure TPU (curve B in Figs. 2 and 4) and pure CTPU (curve C in Figs. 6 and 8) are ascribed to the melting of poly(caprolactone) segments at around 313 K. The addition of SANs does not significantly influence T_m values in either TPU or CTPU.

In DSC curves, the glass transitions of the hard segment ($T_{g,\mathrm{hard}}$) of TPU and CTPU were not found. With addition of SAN1 or SAN2 (more than 25 wt%) to TPU (Figs. 3 and 5) and CTPU (Figs. 7 and 9), a new glass transition appeared, which may be due

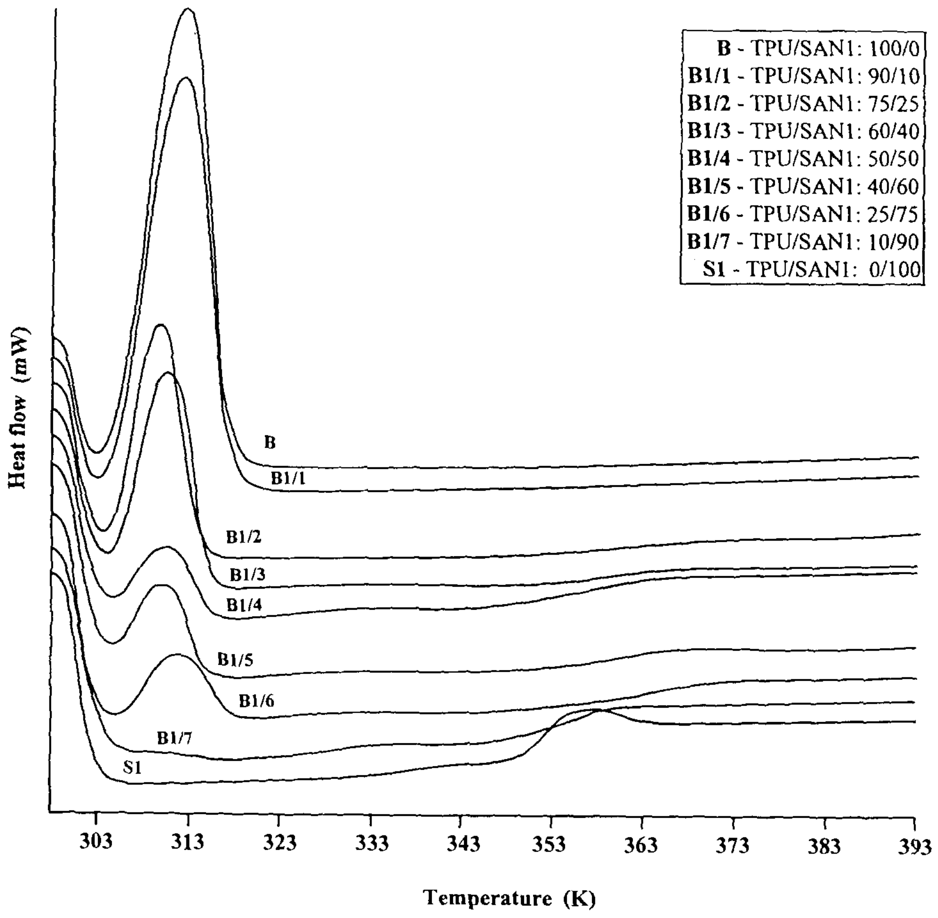

Fig. 2. Curves of T_m values of TPU/SAN1 blends.

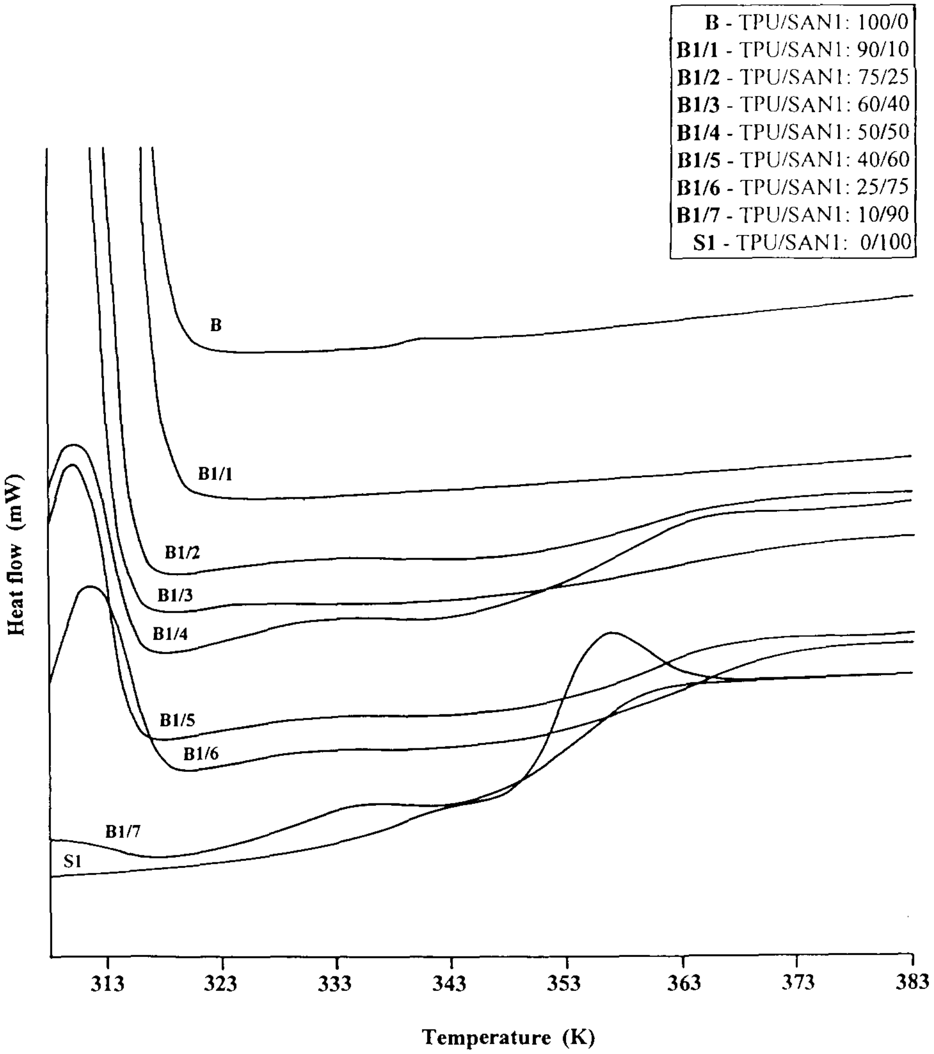

Fig. 3. Curves of $T_{g,\text{hard}}$ and $T_{g,\text{SAN}}$ values of TPU/SAN1 blends.

to the value ascribed to the TPU or CTPU hard segments. This phenomenon can be explained by a strong separation of hard and soft segments in TPU and CTPU. The rigid-hard segments are determined with interchain interactions. Phase segregation may be the result of incomplete miscibility of hard and soft segments of TPUs or two polymers in solution. It may be caused by the crystallization of the hard segment of TPU or CTPU. The structure of TPU also has an impact on the $T_{g,\text{hard}}$ values; all values are higher for CTPU/SANs.

Curve S1 (Figs. 3 and 7) shows $T_{g,\text{SAN1}}$ values of pure SAN1 (358 K), and curve S2 (Figs. 5 and 9) $T_{g,\text{SAN2}}$ values of pure SAN2 (353 K). DSC thermograms show that $T_{g,\text{SAN}}$

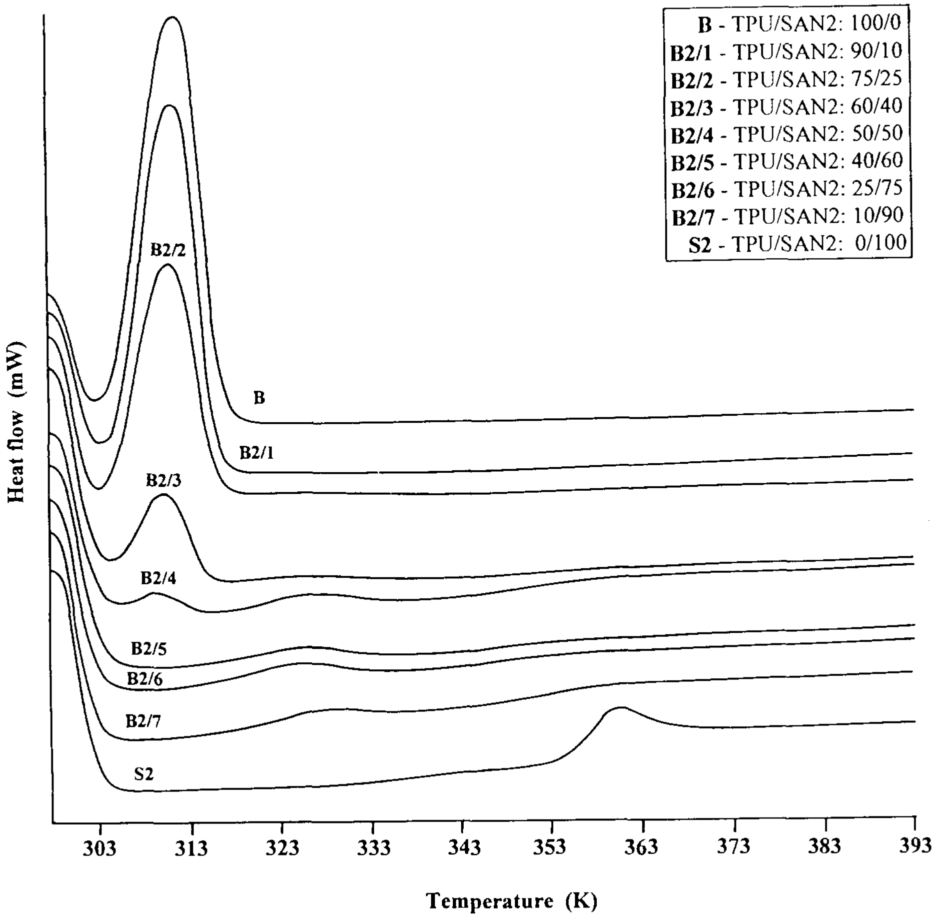

Fig. 4. Curves of T_m values of TPU/SAN2 blends.

values increase with increasing the amount of TPU or CTPU in the blends, and they are lower in TPU/SANs blends than in CTPU/SANs blends.

3.2. *Calculation of interactions in blends of TPU/SAN and CTPU/SAN*

Calculated interaction parameters (χ_{12}) of TPU/SANs and CTPU/SANs blends are presented in Table 1.

From Table 1, it can be seen that the blends of TPU with SAN1 and SAN2 have higher χ_{12} than blends of CTPU with SAN1 and SAN2. Within the entire composition range, TPU/SAN1 blends have higher χ_{12} values than TPU/SAN2 blends, except for the composition at 60:40 where they are approximately the same. The χ_{12} of CTPU/SAN1 blends are lower than the χ_{12} of CTPU/SAN2 blends. Minimal χ_{12} for

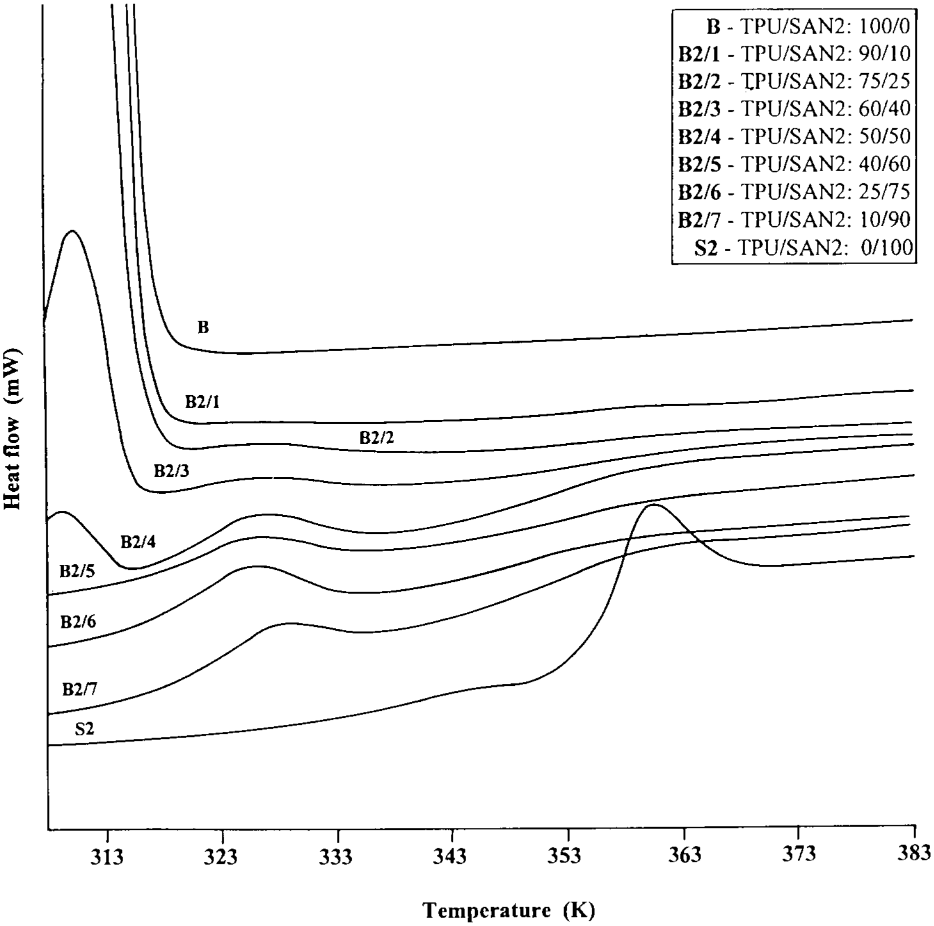

Fig. 5. Curves of $T_{g,\mathrm{hard}}$ and $T_{g,\mathrm{SAN}}$ values of TPU/SAN2 blends.

TPU/SANs and CTPU/SANs blends were found for the compositions between 75:25 and 60:40. The χ_{12} value seems to depend on the amount of AN component in SANs and also on the chemical structure of TPUs. Vanneste and Groeninckx [16] came to similar conclusions. It is also evident that χ_{12} values are higher in the blends where SAN1 or SAN2 is the matrix and TPU is the dispersed phase.

The Scott equation was used to calculate the critical χ_{12} [16,17]

$$(\chi_{12})_{\mathrm{cr}} = \frac{(x_1^{-1/2} + x_2^{-1/2})}{2} \tag{5}$$

The parameter $(\chi_{12})_{\mathrm{cr}}$ depends on the molar mass of polymer; x_1 and x_2 are the degrees of polymerization of polymers 1 and 2. The values of the degree of polymeriz-

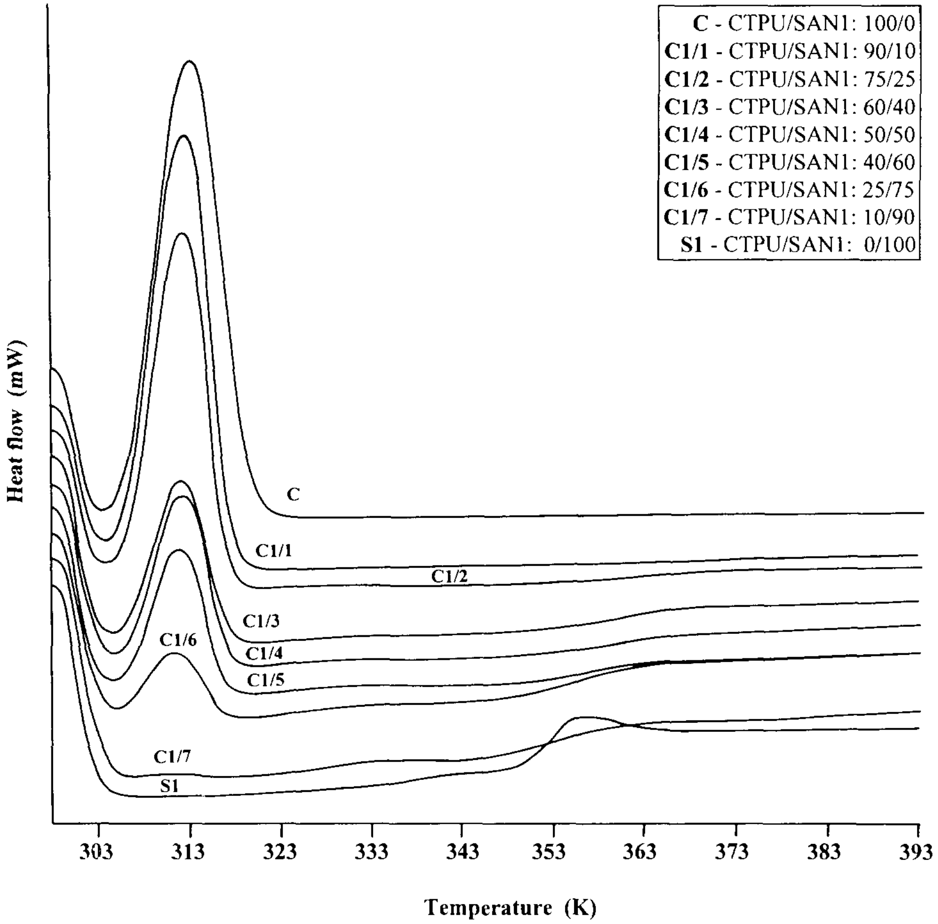

Fig. 6. Curves of T_m values of CTPU/SAN1 blends.

ation (x_1, x_2) are equal to the molar mass of polymers 1 and 2 (M_{n1}, M_{n2}). $(\chi_{12})_{cr}$ for high molar mass polymers tends to be zero. According to Krause, χ_{12} and $(\chi_{12})_{cr}$ are correlated by the following inequalities determining the state of a polymer–polymer system [17]

$\chi_{12} > (\chi_{12})_{cr}$: the system is unstable and separates into two phases,

$\chi_{12} < (\chi_{12})_{cr}$: the system is stable.

Calculated $(\chi_{12})_{cr}$ values for the systems of TPU/SANs and CTPU/SANs blends are given in Table 2.

From the results presented in Table 2, it was found that χ_{12} values for TPU and CTPU blends with SANs are higher than $(\chi_{12})_{cr}$, which is indicative for partially miscible or immiscible blends and also leads to the conclusion that blends separate into two phases.

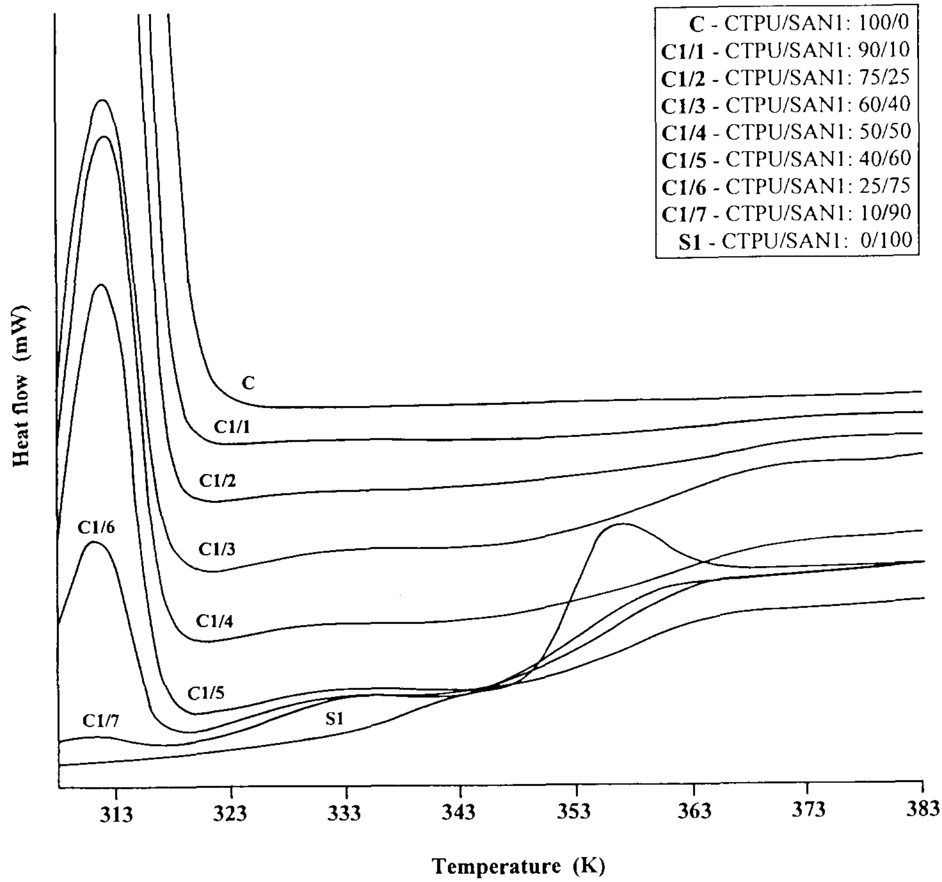

Fig. 7. Curves of $T_{g,\mathrm{hard}}$ and $T_{g,\mathrm{SAN}}$ values of CTPU/SAN1 blends.

Table 1
Calculated averaged interaction parameter (χ_{12}) of TPU and CTPU blends with SANs.

Composition of blend (g/g)	Averaged interaction parameter (χ_{12}) (10^{-5})			
	TPU/SAN1	TPU/SAN2	CTPU/SAN1	CTPU/SAN2
100/0				
90/10	2.21	2.18	2.14	2.14
75/25	1.94	1.93	1.87	1.87
60/40	1.93	1.95	1.88	1.89
50/50	2.04	2.03	1.95	1.97
40/60	2.17	2.17	2.08	2.09
25/75	2.50	2.42	2.38	2.41
10/90	3.29	3.22	3.08	3.10
0/100				

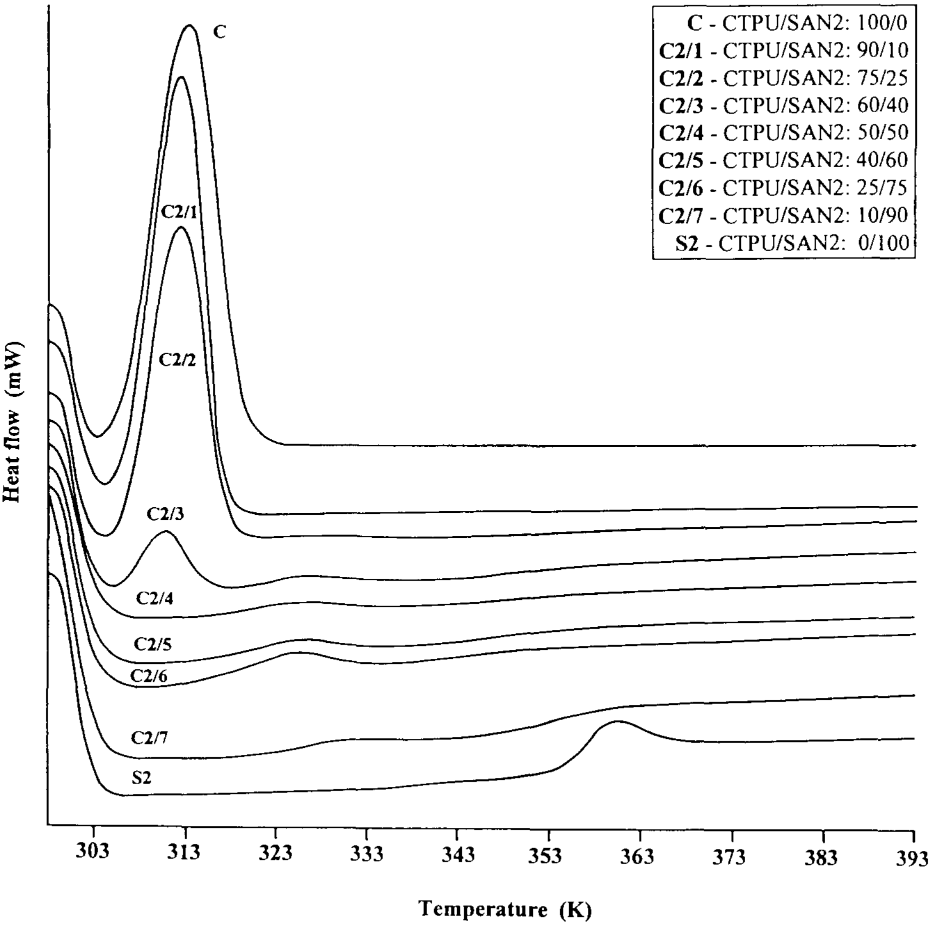

Fig. 8. Curves of T_m values of CTPU/SAN2 blends.

Table 2
Critical interaction parameter $(\chi_{12})_{cr}$ for the systems of TPU/SANs and CTPU/SANs blends

Critical interaction parameter	Blend			
	TPU/SAN1	TPU/SAN2	CTPU/SAN1	CTPU/SAN2
$(\chi_{12})_{cr}$ (10^{-5})	1.61	1.59	1.57	1.56

The condition $(\chi_{12})_{cr}/\chi_{12} = 1$ corresponds to the transition of a polymer–polymer system from a stable to a metastable state [16]. The values of the ratio $(\chi_{12})_{cr}/\chi_{12}$ for the TPU/SANs and CTPU/SANs blends is close to 1 only for compositions at 75:25 and 60:40.

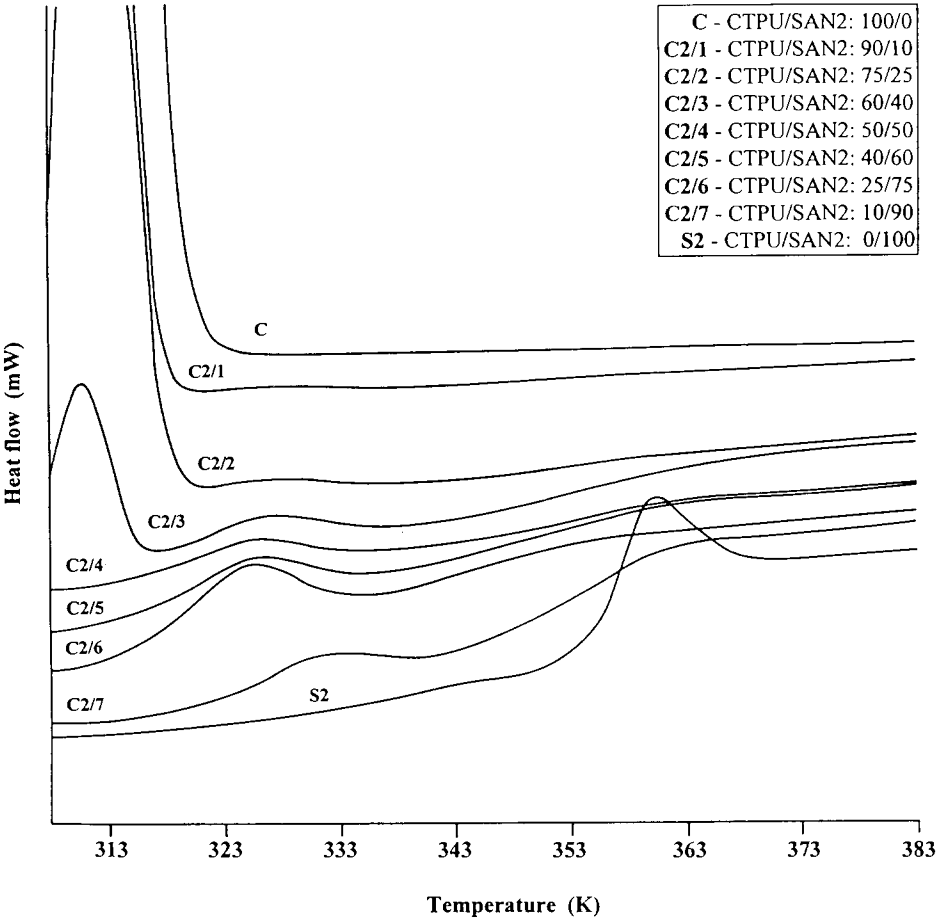

Fig. 9. Curves of $T_{g,\mathrm{hard}}$ and $T_{g,\mathrm{SAN}}$ values of CTPU/SAN2 blends.

4. Conclusions

The changes in structure of TPU and CTPU soft segments are expressed by different values of $T_{g,\mathrm{soft}}$ for TPU and CTPU. However, the values of $T_{g,\mathrm{soft}}$ are also dependent on the amount of AN component in SANs. In pure TPU and CTPU, glass transition of the hard segments was not found. With addition of SAN1 or SAN2 (more than 25 wt%) to TPU and CTPU, the new glass transition appears. T_m values of pure TPU and CTPU are associated with the melting of poly(caprolactone) segments. The addition of SANs does not significantly affect the T_m values. $T_{g,\mathrm{SAN}}$ values increase with increasing amount of TPU or CTPU in the blends, and they are lower in TPU/SANs blends.

Blends of TPU/SANs and CTPU/SANs have the minimum of calculated χ_{12} for compositions at 75:25 and 60:40. The values of χ_{12} of blends are influenced by the amount of AN component in SANs and the chemical structure of TPU or CTPU.

Interactions are stronger in the composition range where SAN1 or SAN2 is the matrix and TPU or CTPU is the dispersed phase.

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