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INTERACTION BETWEEN POLYMERS

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INTRODUCTION

Polymer blends have been a topic of importance in material science during recent years. This is because blending of different polymers can result in new materials with advantageous properties having great potential for new applications. Most of the work done on this subject has been focused on blends of flexible macromolecules [1]. The classic Flory-Huggins theory [2] and extensions of this model [3, 4] have been most helpful for understanding phase behavior. Miscibility is understood as the penetration of components on the molecular level, analogous to low molecular weight substances. Fundamentally, one describes the miscibility of two arbitrary components thermodynamically by the Gibbs free energy of mixing ΔG^M:

$$\Delta G^M = \Delta H^M - T\Delta S^M \tag{1}$$

where ΔH^M is the enthalpy of mixing and ΔS^M is the entropy of mixing.

Any two components are mutually miscible if the mixing free energy of the systems meets the following conditions:

$$\Delta G^M < 0 \tag{2}$$

$$\left(\frac{\partial^2 \Delta G^M}{\partial \phi^2}\right)_{p,T} > 0 \tag{3}$$

ϕ is the molar fraction of one component.

The condition $(\Delta G^M)' > 0$ means mathematically that $\Delta G^M(\phi)$ is a convex function of the composition of the mixture (ϕ).

This results in the well-known phase separation diagram with LCST or UCST, binodal and spinodal. But most of the polymers are not miscible with one another, so that a thermodynamic description is not possible since the phase separation diagram cannot be determined. This "chemical incompatibility" results in many cases in a stable finely dispersed distribution of polymers in one another. The dispersity (or the particle size) correlates with the interactions in the interfaces and with further states of order in the polymers.

For this reason we discussed [5] the concept of Wu [6] based on the presence of interfaces in multiphase polymer mixtures by using the thermodynamic work of adhesion between two different solids for the description of polymer blends. This specific thermodynamic adhesion energy or, in the case of a known adhesion distance, the specific adhesion strength W_{12} between two solids can be determined from the surface tensions γ_1 and γ_2 and the interfacial tensions γ_{12}:

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{4}$$

The surface tension is the sum of the components γ^d and γ^p:

$$\gamma = \gamma^d + \gamma^p \tag{5}$$

where γ^d is the apolar disperse and γ^p the polar component. The interfacial tension γ_{12} between the polymers can be calculated from the surface tensions and their components:

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1{}^d\gamma}{\gamma_1{}^d + \gamma_2{}^d} - \frac{4\gamma_1{}^p\gamma_2{}^p}{\gamma_1{}^p + \gamma_2{}^p} \tag{6}$$

Equation (6) is only valid provided that no reaction takes place between the polymers. But in most practical cases, modifications of the phases are undertaken to initiate reactions. Here, the precise chemical composition of the interface is unknown. This calculation is possible by means of the statistical mechanics of the interfaces introducing the Flory-Huggins parameter χ, the mean coil radius, and the degree of polymerization [7]. The Flory-Huggins parameter can be measured from the surface tensions in the melt and by inverse gas chromatography. But it is not easy to measure χ exactly. In these cases it is possible to calculate the interfacial tensions from measurements of the thickness of the interfaces. This results in an inverse proportionality of the interfacial tension to the thickness of the interlayer L according to Wu [8].

Helfand and coworkers defined two parameters for the interdiffusion of two polymers:

Parameter B for polymer j:

$$B_j = \frac{1}{6}\rho_{0j}b_j^2 \tag{7}$$

where ρ_{0j} = density of the pure component
b_j = statistic segment length according to $b_j^2 r_j = \langle R^2 \rangle_j$
r_j = degree of polymerization
$\langle R^2 \rangle_j$ = mean coil diameter

Parameter α for polymer j:

$$\alpha = \rho_{0j}\chi \tag{8}$$

Wu defines the thickness of interface L and the interfacial tension γ_{12} for polymers with high interaction forces, e.g., by chemical reaction:

$$L = 2\left(\frac{B_1^2 + B_2^2}{2\alpha}\right)^{1/2} \tag{9}$$

$$\gamma_{12} = \frac{2}{3}kT\alpha^{1/2}\frac{B_1^3 - B_2^3}{B_1^2 - B_2^2} \tag{10}$$

After elimination:

$$\gamma_{12} = \frac{(2)^{3/2}}{3}\frac{kT}{L}\frac{(B_1^3 - B_2^3)(B_1^2 + B_2^2)^{1/2}}{B_1^2 - B_2^2} \tag{11}$$

According to Wu, the empirical equation results:

$$\gamma_{12} = 55L^{-0.86} \qquad (\gamma_{12} \text{ in dyn/cm, } L \text{ in Å}) \tag{12}$$

Furthermore, Wu [8] showed that in mechanical melt mixtures of two polymers, the particle size of the disperse phase depends on the interfacial tension, and on the ratio of the viscosities of the polymers and the shear rate during the mixing process, i.e., on technological parameters. This is well understood, although the correlations formulated by him also depend on the polymer components of the mixture chosen. They do not have a universal character.

We demonstrated [5] that a correlation exists between the difference of the polar component of the interfacial tension and the particle size of the disperse phase and on mechanical properties, if no further interaction occurs, which do not change the surface tension. Thus, this concept is, as expected, not sufficient for a description of polymer blends.

For this reason it is necessary to exclude all technological magnitudes of influence in experimental investigations. This means that if no homogeneous phase exists in the blend, one has to start with a homogeneous mixture via solution in a mutual solvent and evaporation of the solvent below the glass transition temperature of the polymers. After heating the melt of this unstable mixture, the particle size and form of the disperse phase and the thickness of the interface allow conclusions about the thermodynamic state to be made.

In our preceding paper [5] we discussed the possibilities of increasing the compatibility in polymer blends. In this paper we will refer to the preceding one only if it is important for the polymer blends discussed.

It is our opinion that, besides the thermodynamic description of polymer blends, a knowledge of the nature of interactions is of fundamental importance for a description of polymer blends. This may result in novel cognitions. This corresponds with the intention of a chemist to find correlations among the chemical and physical interactions and the macroscopic properties of the blends. This means trying to interpret the terms of enthalpy and entropy contained in Eq. (1) by means of chemical and physical processes.

Experimental proof of the single-phase state or of a homogeneous state depends, respectively, on the resolution of the measuring method used. Olabisi, Robeson, and Shaw [9] described blends as miscible when they show a macroscopic " . . . behavior similar to that expected of a single-phase system. . . . "

We use the glass transition temperature which describes the homogeneity in the region of the segmental order of magnitude (Elias [10], 5 nm; Paul and Newman [11], 35-50 nm). DMA measurements produce well characterized signals involving the glass transition temperature via

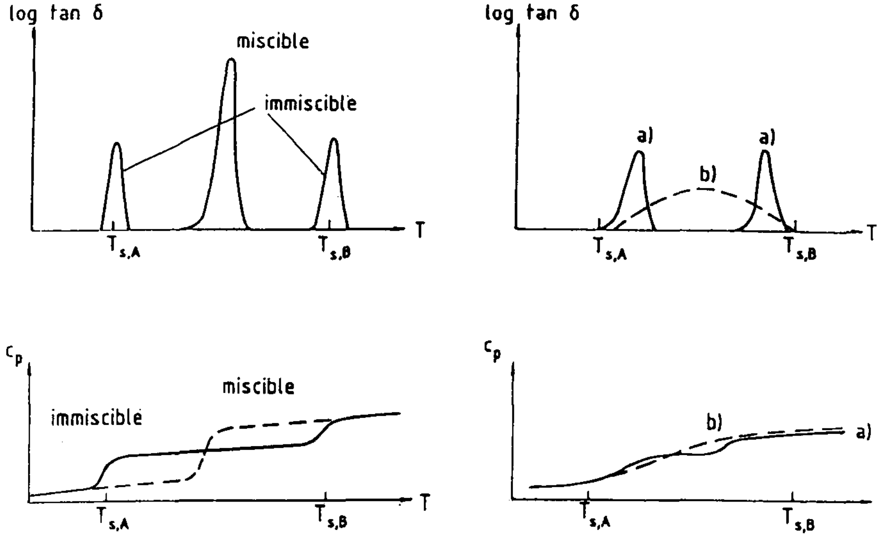

FIG. 1. Typical DMA (log tan δ) and DSC (C_p) signals for a homogeneous, i.e., miscible, and a heterogeneous, i.e., immiscible, blend (consisting of components A and B (left half) and for states of the system named partially miscible (a) and microheterogeneous (b) (right half), respectively).

loss modulus or tan δ. Also well suited are DSC measurements. They also allow a quantification of caloric magnitudes.

Figure 1 schematically shows typical DMA (log tan δ) and DSC (C_p) signals for a homogeneous, i.e., miscible, and a heterogeneous, i.e., immiscible, polymer system with components A and B (left half) and for partially miscible (a) and for phases named microheterogeneous (b), respectively, (right half).

Partially miscible means that a two-phase structure is generated when two polymers are mixed. Both phases contain different but limited amounts of each component.

Microheterogeneous means that a multiphase structure is generated when two polymers are mixed. In the microphase region, homogeneity exists. The distribution function of the composition of these microphases determines the macroscopic properties.

The dependence of phase behavior on temperature and composition was mentioned above.

We now demonstrate our concept by two polymer systems. Blends of different thermoplastics with thermoplastic polyurethanes (TPU) show the influence of additional interactions or chemical bonds on phase behavior and macroscopic properties. Polycarbonate (PC)/polybutene terephthalate (PBT) blends show how the crystallization process of PBT influences the phase behavior of the blends and how the PC content influences the crystallization rate of PBT.

RESULTS AND DISCUSSIONS

1. TPU Blends

Two particularities have to be considered when using TPU as a blend component. On the one hand, TPU is a microheterogeneous polymer, i.e., it is of multiphase structure consisting of hard and soft segments. The mechanical properties of TPU are determined decisively by the distribution of the microheterogeneous hard phases in the soft phases. High shear forces at temperatures just below the T_g of the hard phase initiate a growth of the hard (crystalline) parts at the cost of the smaller particles. Thus, the phase separation is increased, resulting in a reduced interface and, consequently, in a strong decrease of the mechanical properties of the TPU. On the other hand, only in a small number of polymers does a single-phase state occur in blends with conventional thermoplastics above 5 wt% and in the temperature range where TPU is thermostable. For this reason, one has to use the concept of interfacial tension to describe TPU blends. In this case we consider only the polar term of the surface tension: the disperse term is nearly equal for different polymers.

Table 1 summarizes the polar components γ^p of various polymers which we determined by means of contact angle measurements. Table 2 contains the differences of polar components $\Delta\gamma^p$ and the particle sizes a_n of the dispersed phase in TPU polymer combinations as determined by TEM.

The subscript r in Table 2 indicates a chemical reaction in this blend, i.e., grafting between the two polymers. For that to occur, either a peroxidic grafting or the reaction of excess NCO terminal groups with OH or COOH groups of the second polymer was used.

We can see a correlation between the difference of the polar component and the particle size only for combinations of TPU with EVA and TPU with PMMA according to Wu [6]. In all other cases the particle

TABLE 1. Polar Components γ^p of Different Polymers Determined by Contact Angle Measurements

Polymers	γ^p
LDPE	9.5
ABS	11.4[a]
PS	11.6[a]
EVA (medium v.ac.c.)	13.0
SAN	13.8[a]
PMMA	16.4
TPU (Shore D = 60)	17.8
PA-6	20.4

[a] Graphically extrapolated values.

sizes are smaller than expected. The greatest difference between the particle size expected and the one measured by TEM was found for the combinations TPU/ABS and TPU/SAN. Therefore, these systems have been investigated in more detail. As is evident from Fig. 2, between the TPU matrix and ABS or SAN as the dispersed phase, the FTIR-ATR spectroscopy demonstrated a decrease of the hydrogen bonded C=O groups in the TPU matrix with an increase of the AN content in SAN (or ABS)-TPU blends. The result can be explained by a shift of the

TABLE 2. Polymer Combinations

Matrix	Dispersed phase	$\Delta\gamma^p$	a_n (μm)
TPU	ABS	6.4	0.5 to 4
TPU	EVA	4.8	3 to 15
TPU	EVA_r	4.8	3 to 15 (coated)
TPU	SAN	4.0	0.3 to 1.5
TPU	PA-6	2.6	0.1 to 0.2
TPU	PMMA	1.4	0.4 to 1.8
PA-6	TPU	2.6	0.1 to 1
PA-6	TPU_r	2.6	Not measurable
PC	PBT	1.3	Not measurable

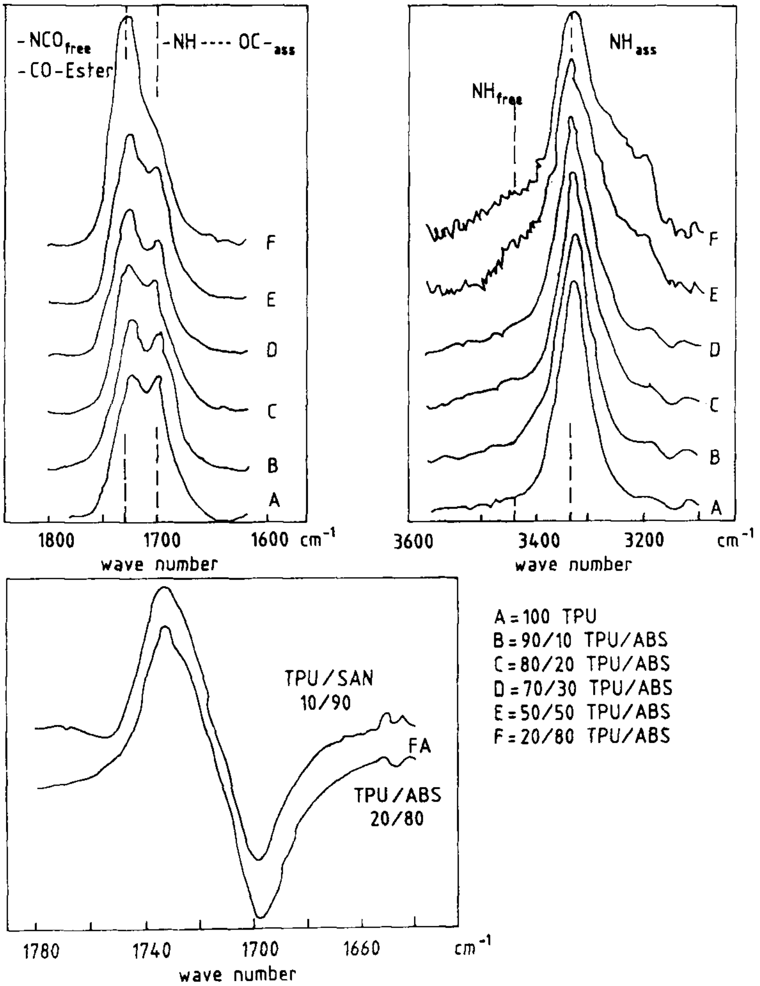

FIG. 2. FTIR-ATR difference spectra of TPU/ABS and TPU/SAN compounds.

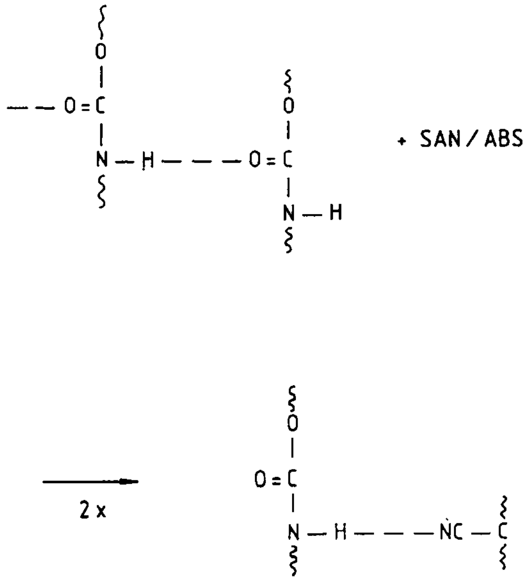

FIG. 3. Shift of the hydrogen bond of TPU/TPU to TPU/SAN or TPU/ABS.

—NH---OC— hydrogen bonds of TPU/TPU to the —NH---NC— hydrogen bonds of TPU/SAN or TPU/ABS as illustrated by Fig. 3. Figure 4 demonstrates the dependence of the shift of the —NH---NC— groups in SAN (or ABS)-TPU blends on the TPU content in the blend. Figure 5 clearly shows the partial miscible character of the T_g values rely on DMA measurements of the tensile loss modulus relaxation curves in TPU/ABS and Fig. 6 in TPU/SAN blends. This phenomenon correlates with an increase in the degree of order in TPU as demonstrated by a change in the glass transition temperature T_g of the soft TPU phase from DSC measurements at low SAN or ABS concentrations (10%) as shown in Figs. 7 and 8. The decrease of the T_g value correlates with an increase of the melt enthalpy of TPU in dependence on the SAN part in the blend as illustrated by Fig. 9. This causes an improvement of the mechanical properties with 10 wt% SAN in TPU at the same time (Table 3). At higher concentrations of SAN (10%), the tensile strength δ_B decreases. In this case the typical structure of TPU is destroyed. That means the phase separation of hard and soft segments and regions of higher order

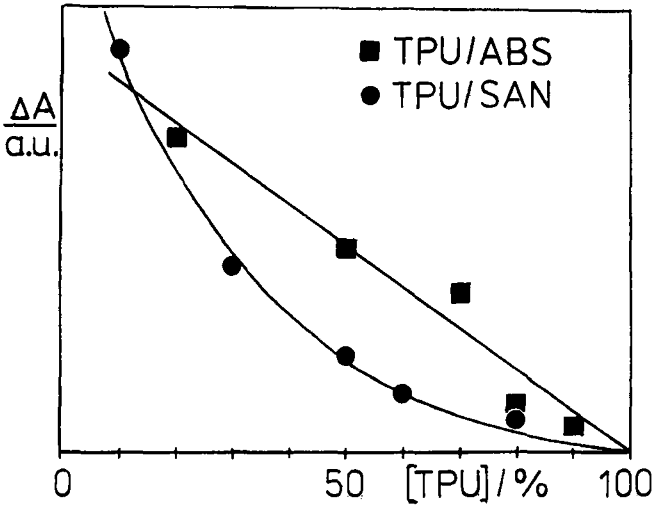

FIG. 4. Shift of the —NH—NC— groups in SAN-(or ABS)-TPU blends in dependence on the TPU content in the blend.

are disturbed. The interactions in the systems TPU/ABS and TPU/SAN can be assumed to be as illustrated by Fig. 10 on the basis of the above measured results.

Joint investigations on the phase behavior of SAN/TPU mixtures by means of light scattering with Kessler and Kammer (TU Dresden) show a typical LCST behavior as shown by Fig. 11. The "homogeneous" TPU phase exhibits a single phase region above 20% SAN (24 wt% AN) and below 200°C by using this measuring method. This is due to the microphase separation in SAN (polar and apolar parts!) and of the TPU (hard and soft segments). The hydrogen bond interaction happens between the polar nitrile sequences (H acceptor) in SAN and the CONH groups (H donor) of the hard phases in TPU. The homogeneity of the mixture is based on the entropic stabilization due to the apolar styrene sequences of the SAN and the soft segments of the TPU in spite of the strong interaction forces (enthalpies): At temperatures above 200°C, the hydrogen bond interaction is reduced so much that phase separation results to both components of the mixture SAN and TPU.

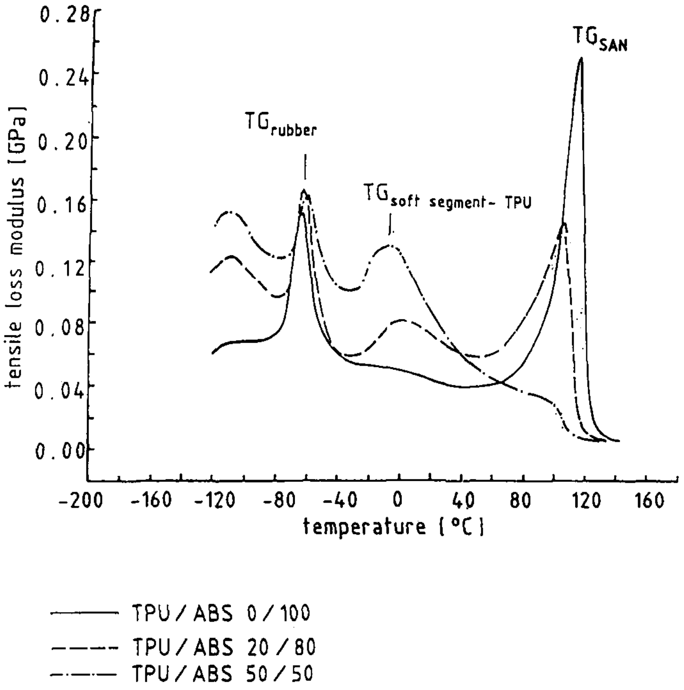

FIG. 5. Influence of TPU admixing on the softening point of the SAN phase TG$_{SAN}$ in ABS.

2. PC/PBT Blends

The experimental results and interpretations concerning PC/PBT blends found in the literature are contradictory. In 1978 Wahrmund, Paul, and Barlow [12] (using Lexan 320 as PC) performed DTA as well as DMA measurements. They found unambiguous and less unambiguous glass transition temperatures. Since the DTA and DMA measurements were performed on differently pretreated samples, a comparison of the results is not exact because the degree of PET crystallization varies. The authors concluded the existence of LCST as well as UCST behavior. They assume the existence of multiple phases whose amount and composition depend on the thermal pretreatment.

Hanrahan, Angeli, and Runt [13] studied blends produced from solu-

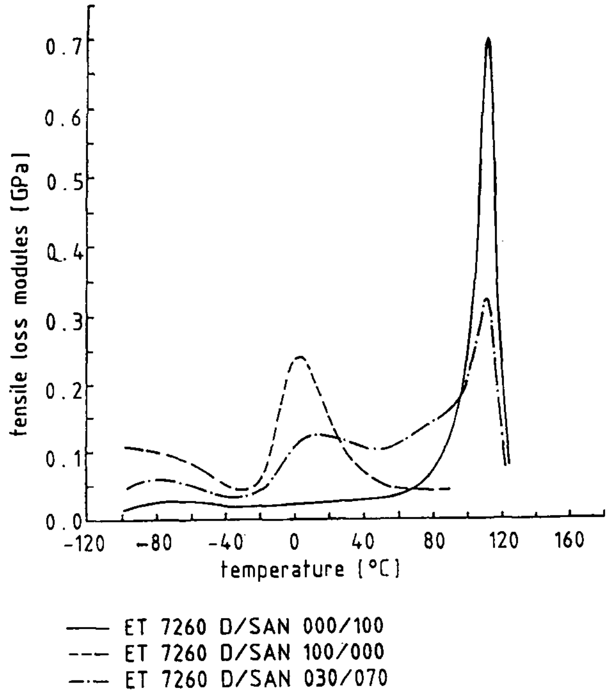

FIG. 6. Comparison of the relaxation curves of ET 7260 D/SAN and of a selected compound.

tion and found them to be completely immiscible. The crystallinity of the PBT was 26 to 38%.

Hobbs et al. [14] found in 1987 for 50 PBT/50 PC (Lexan 141) melt blends a decrease in T_g of 20 K in comparison with the T_g of pure PC. After dissolution and drying, the T_g of the pure PC was found. Therefore, a transesterification reaction can be excluded as the reason for the T_g shift.

Bertillson et al. [15] presented aging experiments with Xenoy (PC/PBT blend) at 130°C and up to 1000 h in their lecture given in Prague in 1989. They concluded there was UCST behavior, i.e., phase separation, followed by completion of the PBT crystallization. Because each crystallization is introduced by a diffusion process, it is not clear whether the first process is a real separation or the beginning of crystallization.

For the following investigations, Bisphenol A-PC (Lexan type 124R/

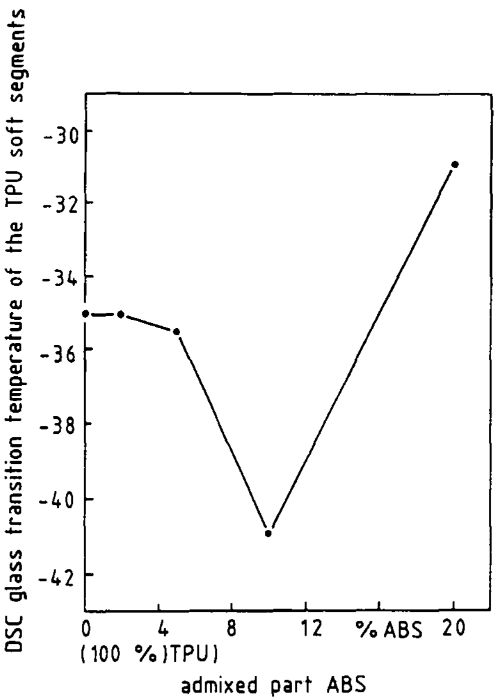

FIG. 7. Influence of ABS admixing on the glass transition temperature of the TPU soft segments (from ΔC_p measurements); TPU type with Shore A = 90.

112, T_g = 141°C) and PBT Grisoplast U ($T_g \approx$ 45°C) were used. The blends were prepared by melt processing in an extruder, followed by injection molding. For the DSC investigations, a Perkin-Elmer DSC 2 was utilized (heating rate: 10 K/min) while DMA measurements were performed by means of a Du Pont DMA 981 (heating rate: 5 K/min).

In Fig. 12 the shear loss modulus is shown to depend on the temperature of the melt blends. A comparison of the mixtures with pure materials exhibits the occurrence of shifts of the glass transition temperature. These changes indicate a certain degree of miscibility. Comparison of the results obtained from the 70 PC/30 PBT and 50 PC/50 PBT samples allows us to recognize that the glass transition temperature of the phase rich in PC has no monotonous change with decreasing PC content. Studying the results of the DSC investigations (Fig. 13) strikingly illustrates that the PC content strongly influences the PBT crystallization.

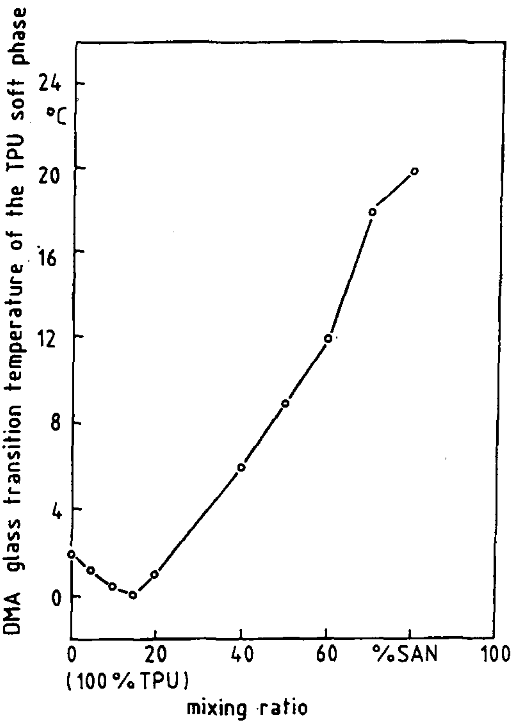

FIG. 8. Influence of SAN admixing on the softening point of the soft segments in ET 7260 D (from E″ measurements).

PBT cold crystallization (above the glass transition range) is essentially stronger in the 70 PC/30 PBT sample than in the 50 PC/50 PBT sample. Analysis of the glass transition temperatures obtained from DSC and DMA measurements is very complicated since more or less unambiguous signals are observed. The dependence of the data on the concentration is presented in Fig. 14. They could be interpreted as the behavior of a possible three-phase system (a phase rich in PBT, a "mixed phase," and a phase rich in PC) similar to the interpretation of Wahrmund et al. [12].

The following section demonstrates the incorrectness of this interpretation.

The samples (initial state) were melted at ~250°C and cooled down slowly so that the crystallization of PBT has a maximum. That can be

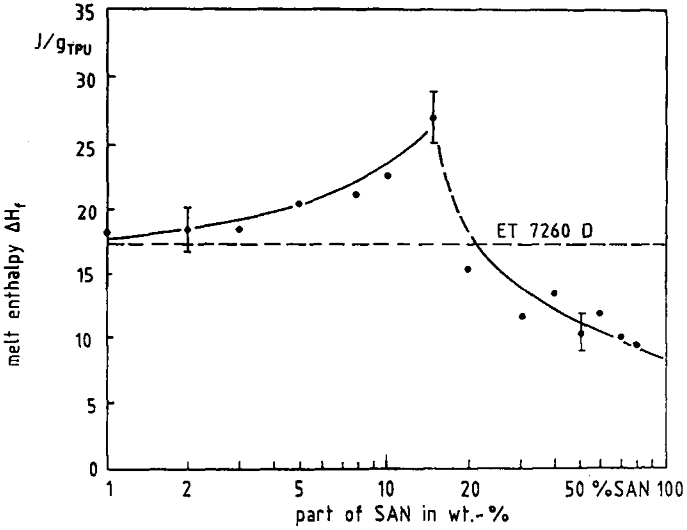

FIG. 9. Melt enthalpy of TPU (ET 7260 D) in dependence on the SAN part in the blend.

proven by DSC measurements (Fig. 15). Only for the 90 PC/10 PBT sample is the PBT crystallization not complete. By a cooling regime such as mentioned above, a nearly pure PC phase is also generated. The T_g values of the PC-rich phase approach the value of pure PC. In the case of a cooling regime for DMA measurements (slower than in the case for DSC investigations), the T_g of pure PC is observed at all blends (Fig.

TABLE 3. Tensile Strength σ_B of TPU/SAN Compounds

Compound		
TPU, wt%	SAN, wt%	σ_B, MPa
100	—	52
90	10	59.5
80	20	48
70	30	39

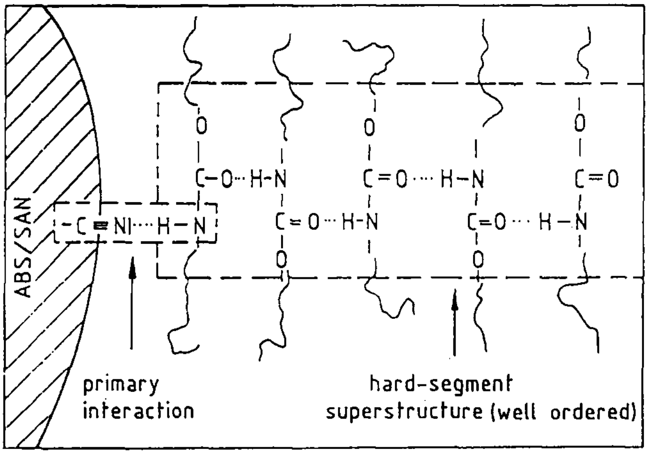

FIG. 10. Scheme of the initiation of the formation of well-ordered hard-segment superstructures from the primary interaction SAN/ABS-TPU.

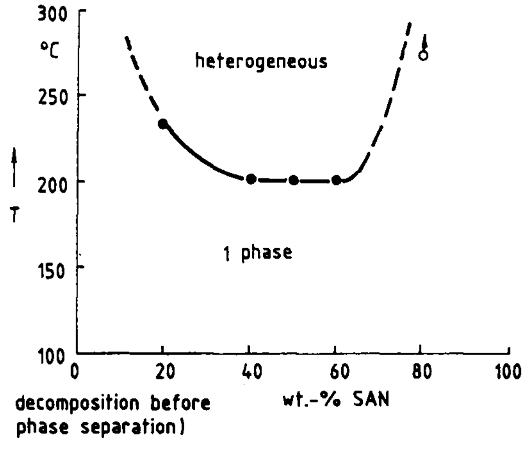

FIG. 11. Phase diagram of TPU (ET 7290 AH) and SAN (AN content 24 wt%) in blends.

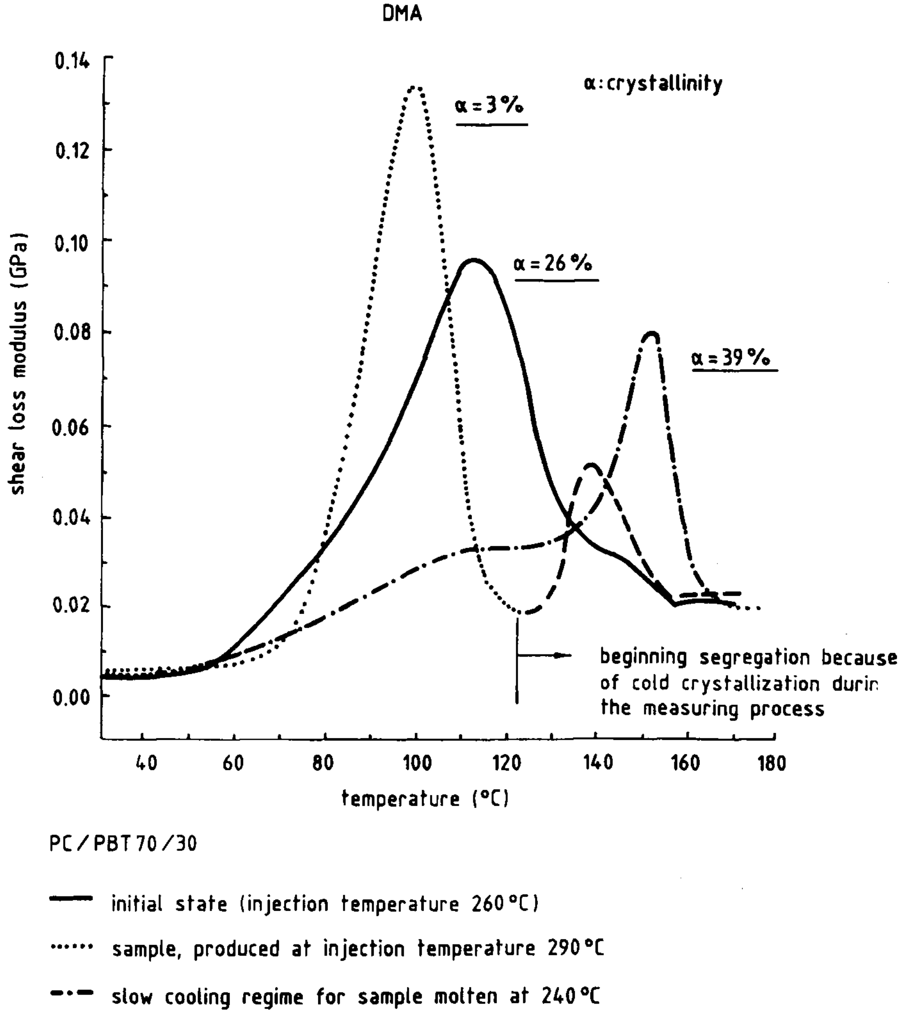

FIG. 12. Shear loss modulus in dependence on temperature for PC/PBT melt blends (initial state).

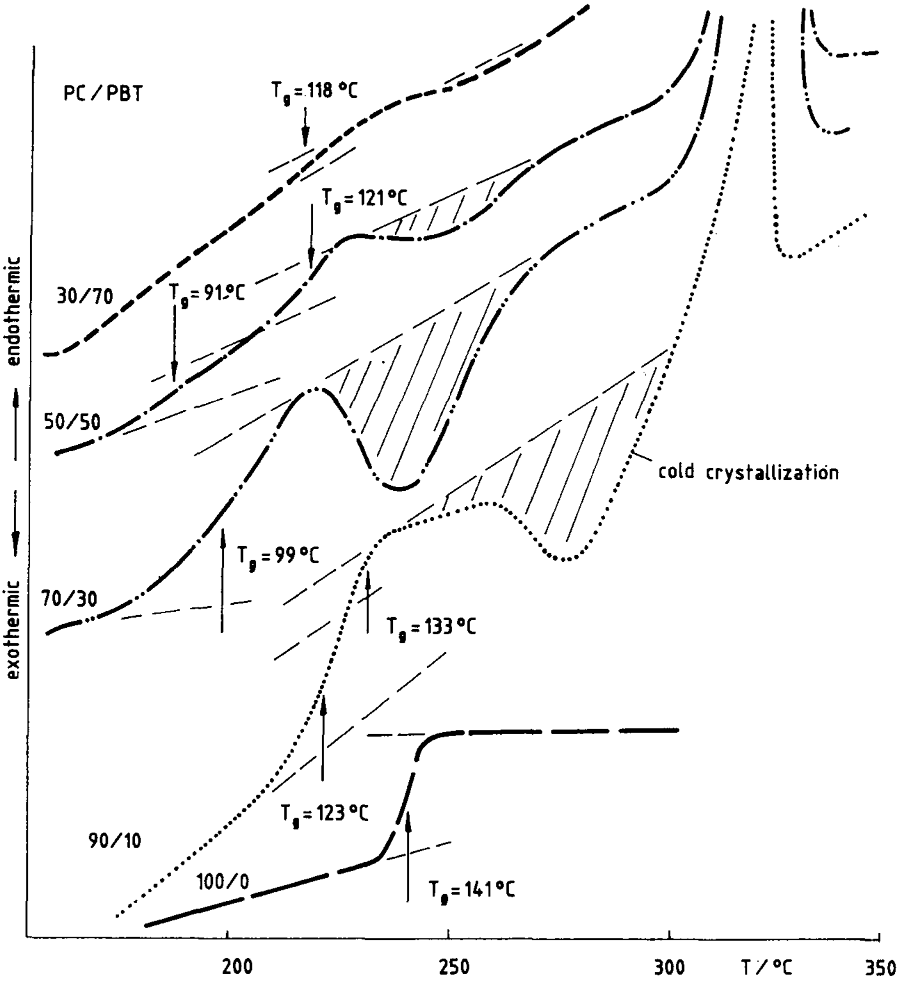

FIG. 13. DSC thermograms for PC/PBT melt blends (initial state).

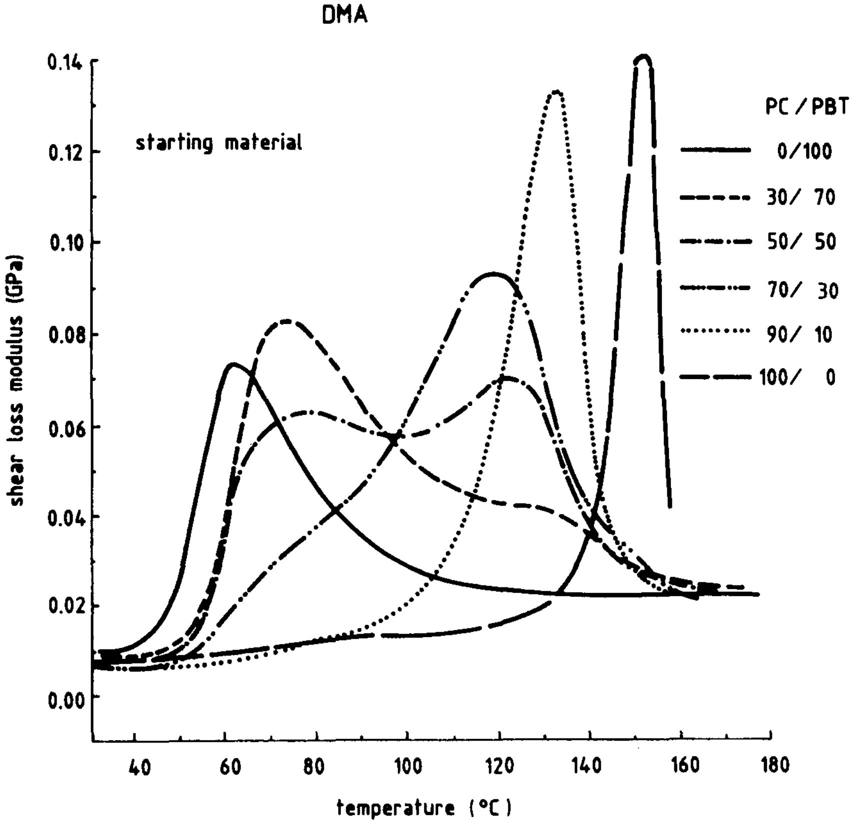

FIG. 14. Dependence of the glass transition temperatures on the composition of specimen in the initial state.

16). The T_g region of the PC phase is followed by a wide region of T_g values smaller than the T_g of pure PC. These results can be explained as an effect of various microphases originating from crystallization. The microphases have a different composition. Thus, the DMA results reflect a distribution function of the composition of the microphases. Comparison of DMA and DSC measurements is evidence that the DSC heating curves give only information on the glass transitions of the PC-rich phase. However, a broad T_g region cannot be clearly detected by means of DSC.

The change of glass transition behavior induced by various degrees of

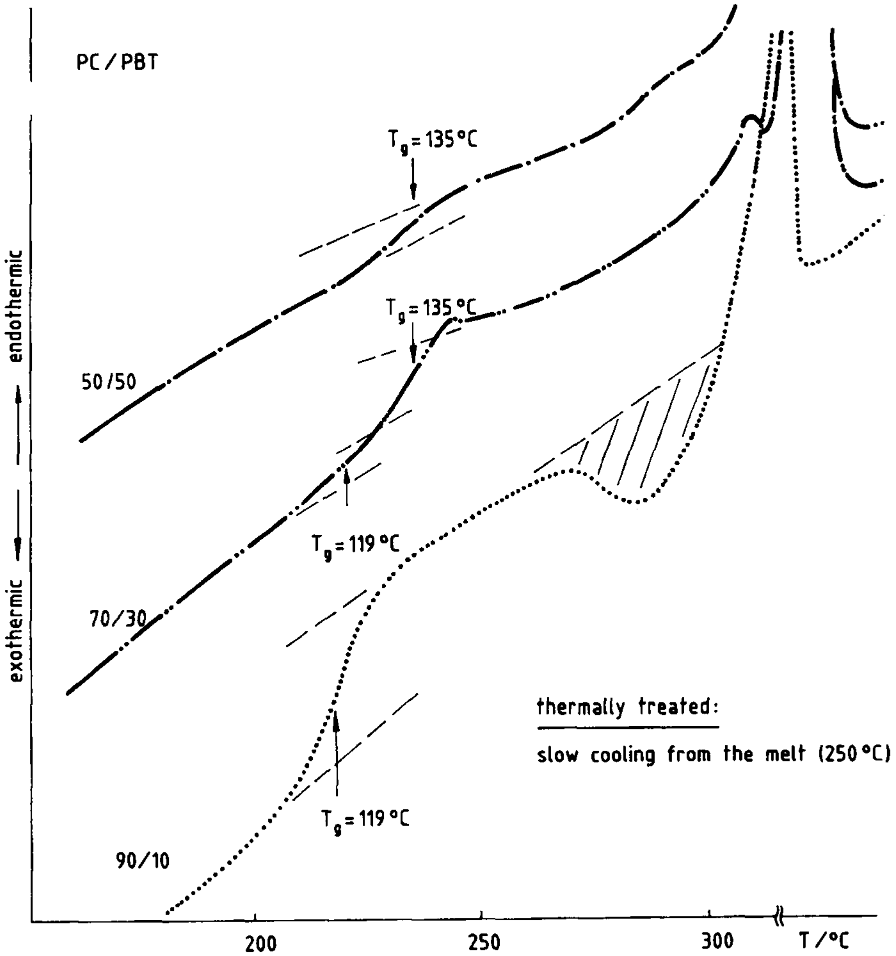

FIG. 15. DSC thermograms after a slow cooling process for PC/PBT blends, molten at 250°C.

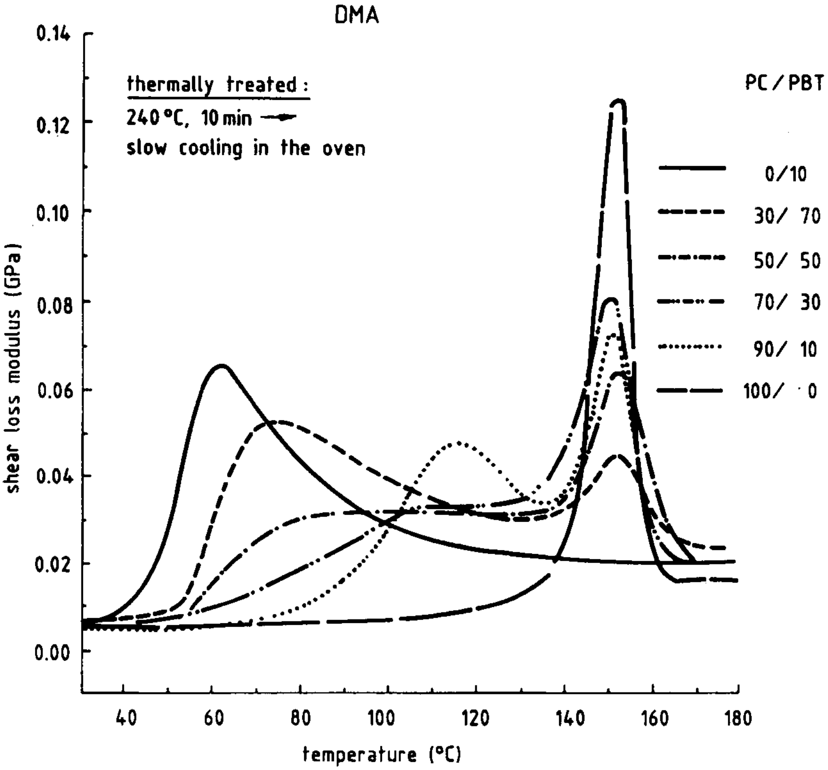

FIG. 16. Shear loss modulus in dependence on temperature after a slow cooling process of PC/PBT blends, molten at 240°C.

PBT crystallinity is clearly visible for the 70 PC/30 PBT sample. Figure 17 represents the DMA results. The degree of crystallinity α varies in its dependence on the preparation and cooling conditions from 3% up to nearly 40% of the PBT content. For the nearly amorphous sample ($\alpha \approx 3\%$), the shape of the DMA signal points to a homogeneous structure. Only one significant glass transition is observed. This means, in the sense mentioned in Point 1, that PC and PBT are miscible in the melt and that this miscibility remains in the solid state if PBT crystallization is excluded. PBT cold crystallization starts above the glass transition.

Figure 17 shows a shift of the maximum of the loss modulus to higher temperatures with increasing crystallinity of the PBT (α = 26 and 39%) and the existence of a wide T_g range as well as a pure PC phase in the

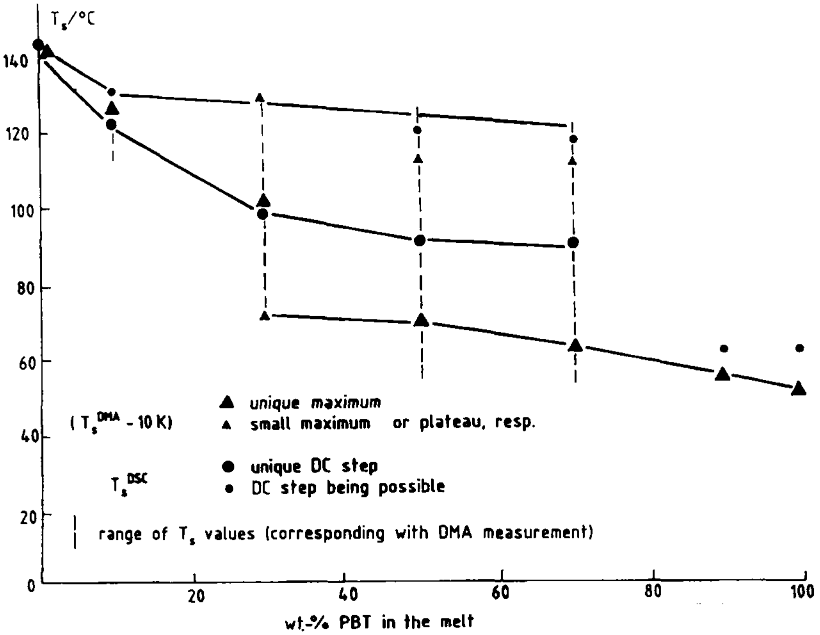

FIG. 17. Dependence of the glass transition temperatures on the composition of specimen in the initial state.

completely crystallized state. Consequently, microheterogeneity in the amorphous phase arises from PBT crystallization.

The glass transition temperatures of the states of the samples with a minimum of PBT crystallinity as well as the glass transition ranges of the samples with a maximum of PBT crystallinity (concerning quantity and size of crystallites) are shown in Fig. 18. Extrapolation of the T_g values of the almost completely amorphous melt mixtures results in the T_g value of 100% amorphous PBT ($T_g = -25$°C) published by Cheng, Pan, and Wunderlich [16].

The results lead to the conclusion that the PC/PBT system is miscible in the sense of the definition given by Olabisi et al. [9] if both components are liquid as well as rigidly amorphous. An early PBT crystallization produced microheterogeneous phases, and the samples did not exhibit further single-phase system behavior.

As a result, we demonstrated that an entropically promoted separa-

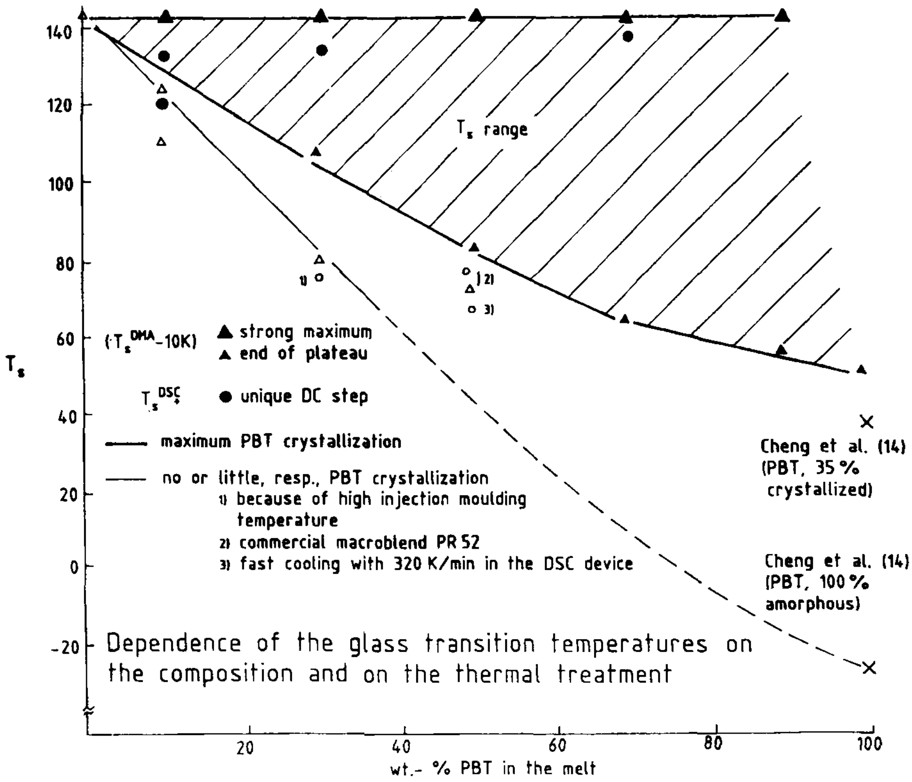

FIG. 18.

tion occurs with increasing PBT crystallization in the case of the PC/PBT blend. Comparable results have been known for some time from the mixing behavior of low molecular weight compounds. Thus, benzene and naphthalene are miscible in every ratio. If naphthalene crystallizes, phase separation of both components occurs. In analogy, phase separation between rodlike liquid crystalline polymers and coiled polymer molecules are entropically promoted. Neither chemically similar main chain polymer structures [17] nor flexible side chains, as compatibility agents [18], result in a homogeneous phase system.

As a result, the demonstrated segregation behavior is shown to be an entropically promoted separation process of the crystalline PBT phase from the amorphous phase. The results concerning PC/PBT blends are in good agreement with Bertilsson, Franzen, and Kubat [19]. Nevertheless, a series of questions is still not answered. This justifies further studies of these interesting blends.

We observed a maximum degree of crystallinity of PBT of 40%. DSC and DMA curves show separation of a PC phase from the crystalline PBT phase. Is the residual amorphous PBT and the PC a homogeneous mixed phase in the blend?

Can a transesterification between PC and PBT be excluded? How do directed transesterified parts affect the phase behavior?

How can a desired microphase distribution be stabilized (see above for TPU) so that no changes occur during processing?

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