Investigation of properties of compatibilized TPU/SAN blends

M.Ulcnik-Krump,[a] * R.Stadler,[b]* T.Malavasic,[a]

[a] National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
[b] MC II, Universität Bayreuth, Universitätstrasse 30, D-95440 Bayreuth, Germany

SUMMARY: The properties of compatibilized thermoplastic polyurethane/ poly(styrene-co-acrylonitrile) (TPU/SAN) blends were investigated. Relaxation temperatures were studied by dynamic-mechanical thermal analysis (DMTA). In comparison, thermal properties were determined by differential scanning calorimetry (DSC). The morphology of the samples was studied by transmission electron microscopy (TEM) .

Introduction

Blending of thermoplastic polyurethane (TPU) and poly(styrene-co-acrylonitrile) (SAN) might be a successful alternative to obtain a new material with good properties. By blending TPU with SAN many different properties can be obtained due to the numerous possible combinations of different polyurethanes (character of hard and soft segments, domain separation, etc.) with different SAN copolymers (weight % of acrylonitrile and different distributions of styrene and acrylonitrile). TPU/SAN blends are known to be immiscible in the whole composition range.[1-3)] In spite of many studies to compatibilize incompatible polymer pairs,[4)] a patent of Van Cleve, Armstrong and Simroth is the only known published work on compatibilization of TPU and SAN.[5)] In the present work the compatiblization of TPU/SAN blends were studied in detail with the goal to improve their miscibility. Taking into consideration many publications[1)] the following polymer additives were expected to act as compatibilizers for immiscible SAN and TPU:

- homopolymers of poly- ε-caprolactone (PCl) with various molecular weights further marked as ***C1x*** (x=a,b,c),
- a mixture of block copolymers polystyrene-block-poly(ε-caprolactone) (PS-b-PCl) and polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) further marked as ***C2***,
- a mixture of block copolymers polyisoprene-block-poly(ε-caprolactone) (PI-b-PCl) and polybutadiene-block-poly(methyl metacrylate) (PB-b-PMMA) further marked as ***C3***.

 CCC 1022-1360/00/$ 17.50+.50/0

Materials and characterization methods

Commercial TPU (Ellastolan C85 A-50) with polyester soft segments and SAN (Luran 386 R) with 20 wt.% of acrylonitrile, supplied by BASF, Ludwigshafen, Germany were used as basic components. Polymers with defined structure, homopolymers and block copolymers used as possible compatibilizers were synthesized via living anionic polymerization. The details of the synthesis were presented elsewhere.[6] Compatibilizers characteristics determined by SEC and ^{1}H-NMR are summarized in Table 1. All blends were prepared from melt at 210°C, using a co-rotating twin-screw mixer with conical screws, developed by the TU Eindoven, Netherlands.

Table 1. Molecular properties of synthesized polymers.

Compatibilizer denotation	Structure	$M_w \cdot 10^{-3}$ [a] (g/mol)	M_w/M_n [a]	wt.% of A block [b]
C1a	PCl	104	1.31	-
C1b	PCl	87	1.24	-
C1c	PCl	49	1.40	-
C2	PS-b-PCl	65	1.25	30
	PS-b-PMMA	78	1.16	24
C3	PB-b-PMMA	105	1.07	29
	PI-b-PCl	137	1.18	65

[a] Obtained by SEC
[b] Obtained by ^{1}H NMR,
for C2 , A-block = PS;
for C3 , A-block = PB or PI

The calorimetric measurements were performed by a Perkin-Elmer DSC 7 under a dry nitrogen atmosphere. Measurements were made separately in the high and in the low temperature range at a heating rate of 20°C/min. The dynamic mechanical measurements were performed by a Rheometrics DMTA IV at a constant frequency of 10 rad/s, using the thin film fixture. The temperature was varied from –140°C until sample failure at a heating rate of 2°C/min.

The sections of compatibilized and non-compatibilized TPU/SAN 25/75 blends were cut with a Reichert cryoultramicrotom at -60°C using a diamond knife. All samples were stained with a 4 wt.% aqueous solution of phosphotungstic acid. Micrographs were taken with a CEM 902 Zeiss transmission electron microscope, with accelerating voltage of 80 kV.

Thermo-mechanical and thermal properties

In order to investigate the compatibility of the different compatibilizers proposed, blends of TPU or SAN with 20% of each compatibilizer (border conditions) were investigated. Figs.1.a and b display the changes of tan(δ) (tan(δ)=E"/E' where is E' the storage modulus and E" the loss modulus) vs. temperature for SAN/Cx and TPUCx 80/20 blends, respectively. Curves are shifted along the ordinate axis to prevent the overlap of data points. The addition of different compatibilizers influences thermal and thermo-mechanical properties of SAN, while for TPU no pronounced dependency on any added compatibilizer was found. The change of glass transition temperature (T_g) of SAN (in comparison with T_g of pure SAN) was maximal for the SAN/C1x blends. The addition of C2 decreased T_g of SAN, what was ascribed to the PCl block of the compatibilizer, but no pronounced influence of PMMA block on SAN properties was found. As concerns the SAN/C3 blend, two additional relaxations were observed. The first relaxation at approximately –70°C corresponds to the T_g of the PI-block and indicates the formation of independent separated phases of both block copolymers in the SAN matrix. The second relaxation at approximately 60°C, appearing also in the SAN/PCla and SAN/C1b blends, was probably due to T_m of PCl indicating that pure micro domains of the PCl-block, incompatible with SAN were formed. Another possible explanation in the case of SAN/C2 and SAN/C3 blends is that the PCl block does not mix with SAN due to its connectivity to either PS or PI. However, it has been shown that SAN properties depend on the M_w and the amount of the added PCl. In the TPU/Cx 80/20 blend the T_g of TPU soft segments decreased less than 4°C. For TPU/C2 and TPU/C3 blends an additional weak relaxation at approximately 60°C was observed. It was attributed to T_m of PCl. Therefore, it was assumed that undesirable independent PCl microdomains in the TPU matrix of TPU/C2 and TPU/C3 blends are formed. Their formation may be the consequence of immiscibility of TPU soft segments and these block copolymer mixtures.

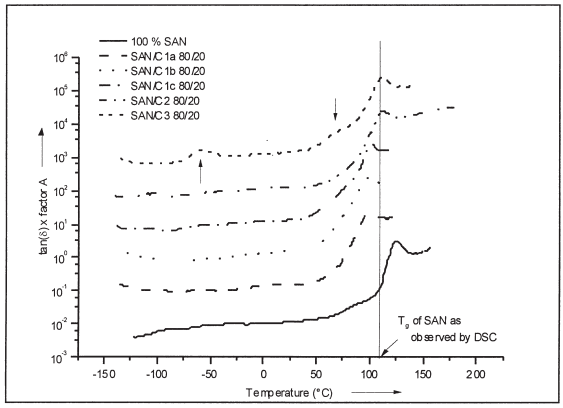

Fig.1a: Tan(δ) for SAN and SAN/Cx 80/20 blends.

The T_g of TPU soft segments and of SAN as obtained by DSC and DMTA measurements for non-compatibilized and compatibilized TPU/SAN 25/75 blends are summarized in Table 2. The results are in agreement with results observed for the border conditions discussed before. The addition of C1x causes bigger changes of T_g of SAN than the addition of C2 or C3 (mixtures of block copolymers). Thermal and thermo-mechanical properties of TPU in the TPU/SAN 25/75 blend seemed not to be influenced by any added compatibilizer. The changes of T_g of TPU soft segments caused with addition of different compatibilizers are small and within the error limits of DSC measurements. Due to the standard deviation up to ±1.8°C for results obtained by DMTA, it can be concluded that added compatibilizers caused only a small decrease of the glass transition temperature of TPU in the TPU/SAN 25/75 blends.

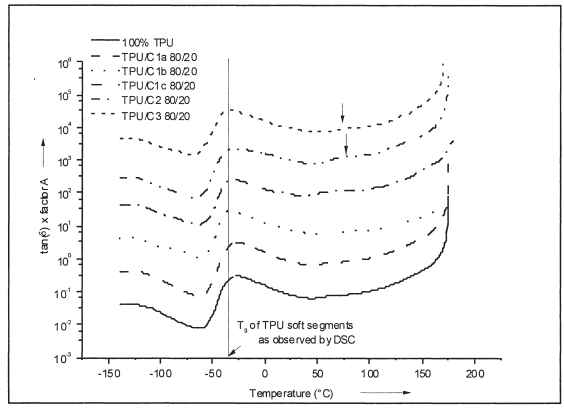

Fig.1b: Tan(δ) for TPU and TPU/Cx 80/20 blends.

Table 2. T_g (α relaxation) of TPU soft segments and T_g (α relaxation) of SAN of TPU/SAN 25/75 blends with 5 wt.% of different compatibilizer.

TPU/SAN 25/75 + 5 wt.% compatibilizer	DSC		DMTA			
	T_g		TPU α-relaxation		SAN α-relaxation	
	(°C)		(°C)		(°C)	
	TPU soft segments	SAN	E''	tan (δ)	E''	Tan (δ)
none	43.7 ± 0.3	105.8 ± 1.0	-37.2 ± 1.0	-36.5 ± 1.3	105.1 ± 1.0	115.5 ± 1.4
C1a	-46.0 ± 0.3	93.0 ± 1.0	-40.5 ± 0.5	-38.8 ± 1.5	94.0 ± 1.0	107.6 ± 1.6
C1b	-45.8 ± 0.4	91.6 ± 1.0	-41.0 ± 1.0	-37.9 ± 1.3	89.0 ± 1.0	104.3 ± 1.3
C1c	-47.7 ± 0.9	95.0 ± 1.1	-40.3 ± 0.3	-37.3 ± 1.3	96.0 ± 1.1	107.0 ± 1.4
C2	-467 ± 0.8	101.1 ± 1.0	-41.2 ± 0.4	-39.0 ± 1.4	102.2 ± 0.9	111.5 ± 1.4
C3	-46.3 ± 1.0	99.9 ± 0.9	-41.2 ± 0.2	-38.4 ± 0.2	101.6 ± 0.4	109.2 ± 0.2

**Values in table are $\bar{x} \pm s$ where $\bar{x}$ is the average value of measurements and s is the standard deviation.

Morphology

In Fig.2 the TEM micrograph of the non-compatiblized TPU/SAN 25/75 blend is shown. The matrix (continuous dark phase) formed by the major component SAN (75 wt.%) and a disperse (discontinuous light phase) TPU phase can be seen demonstrating clearly that TPU and SAN form an incompatible blend. The size and shape of the TPU domains are not uniform. It was presumed that this is the consequence of insufficient equilibrium between coalescence and drop break-up what could also partly reflect the blending conditions (screw speed, temperature, order of adding components into mixer).

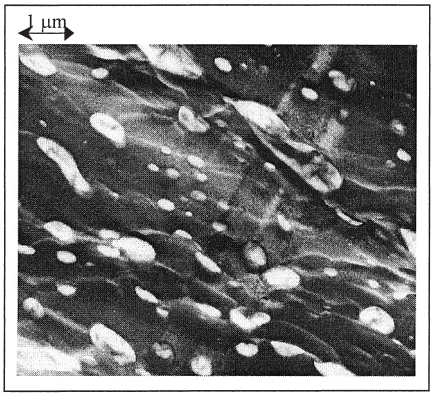

Fig.2:TEM micrograph of TPU/SAN 25/75 blend without compatibilizer.

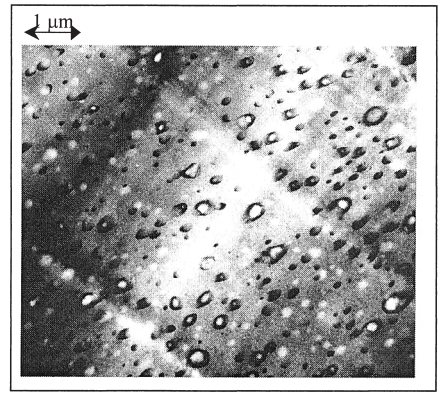

Fig.3: TEM micrograph of TPU/SAN blend with 5.wt.% of C1c.

The boundaries between the TPU and the SAN phases are not sharp. It is evident in Fig. 3 that the addition of PClc causes a large decrease in the size of the TPU domains. Additionally at the TPU-SAN interphases a layer of PClc with indistinct boundaries is clearly seen. The effect of the compatibilizers on the morphology of the TPU/SAN 25/75 blends was further investigated on the basis of distribution of the domain sizes. Areas of each particle were measured and the particle radius, assuming that all particles images are circles, determined. As an example a histogram of a typical non-compatibilized blend is shown in Fig.4.

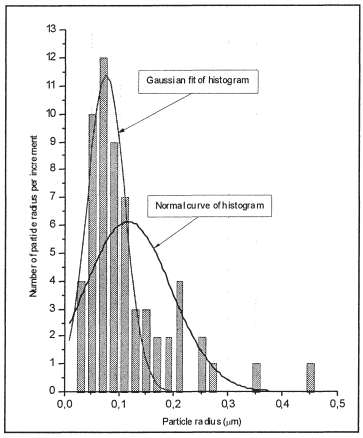

Fig.4: Histogram of typical of TPU/SAN blend without compatibilizer.

The corresponding curves of the normal distributions are shown in Fig.5. The influence of the molecular weight of C1x on the morphology of the blends can be clearly seen. The increase of the size of the dispersed TPU-domains indicates that C1a causes a coalescence, while the addition of C1c (PCl with the lowest molecular weight) reduces the size of the dispersed TPU-domains. Moreover, a narrower distribution of the domain sizes was obtained with the addition of C1c. The size of the dispersed TPU-domains increases in blends compatibilized with C2 and C3, if compared with the non-compatibilized blends. That indicates that C2 and C3 do not stabilize the morphology against coalescence

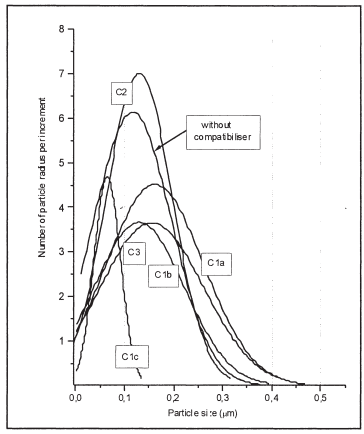

Fig.5: Curves of normal distribution obtained from histograms.

Summary

Thermal, thermo-mechanical properties and morphology of the non-compatiblized and compatibilized TPU/SAN blends were studied. The efficiency of the C1x (PCl homopolymer) depends on the molecular weight (M_w) of the polymer. Addition of the PCl with the lowest M_w lead to a fine dispersed morphology of the blend and gave the best results as compared to the other compatibilizers used in this study. With the addition of C2 (P(S-b-PCl)+P(S-b-MMA)) only the changes caused by the PCl block were noticed while PMMA seemed to have no influence. In the case of added C3 (P(I-b-Cl)+P(B-b-MMA)) undesirable independent phases of block copolymer in the SAN matrix were assumed to be formed. In general, the thermal and thermo-mechanical properties and morphology depend on the total amount and M_w of the added PCl.

References

1B.Zerjal, T. Malavasic, Blends (Thermoplastic Polyurethane-SAN): Polymeric Materials Encyclopedia, Vol. 1, CRC Press, Inc. (1996) ISBN 0-8493-2470.
2 M.Ulcnik, B.Zerjal, T.Malavasic, Thermochim.Acta, **276**, 175 (1996).
3 S. Datta, D.J. Loshe: Polymeric Compatibilizers: Uses and Benefits in Polymer Blends, Charl Hanser Verlag, München, (1996), ISBN 3-446-17411-7.
4 R.Van Cleve, G.H.Armstrong, D.W.Simroth, U.S.Pat.4, 350, 780, Union Carbide (1982)
5.M. Ulcnik-Krump, L. de Lucca Freitas, R. Stadler, T. Malavasic, (submitted for publication to Polymer).

Acknowledgement
M.U.Krump acknowledges many discussions with Dr.L.Freitas (Instituto de Quimica, Porto Alegre, Brazil).