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Surface tension, interfacial tension, and morphology in blends of thermoplastic polyurethanes and polyolefins. Part I. Surface tension of melts of TPU model substances and polyolefins

Petra Pötschke[a,*], Jürgen Pionteck[a], Herbert Stutz[b]

[a]*Institut für Polymerforschung Dresden e.V, Hohe Straße 6, D-01069 Dresden, Germany*
[b]*BASF AG, Polymer Research Division, D-67056 Ludwigshafen, Germany*

Abstract

The pendant drop analysis was used to determine surface tensions γ of polymer melts. For thermoplastic polyurethane (TPU) elastomers, which are block copolymers of crystallisable hard segments (HS) and amorphous soft segments (SS), the surface tensions of the different segments in the melt were measured for the first time. As model compounds for the SS polyetherdiols (PEt-diols) and a polyesterdiol (PEs-diol) were used. To suppress the influence of the hydroxyl end groups on the surface properties the diols were either acetylated or chain extended with a diisocyanate. The influence of the molecular weight and the endcapping method was investigated. All TPU segments exhibit higher surface tensions than that measured for polyolefins due to their polar character except the acetylated PEt-diols with γ-values between those of polypropylene and polyethylene. With 48–45 mN/m at 120–165 °C, the highest surface tension was determined for an amorphous HS model. The surface tensions of both PEs-diols are higher than that of the PEt-diol model compounds. While the surface tensions of the acetylated and MDI extended PEs-diols exhibit the same temperature dependence, differences were found between the surface tension of the acetylated and MDI extended PEt-diols, which diminish with increasing molecular weight of the model substances. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Surface tension; Pendant drop analysis; Thermoplastic polyurethane

1. Introduction

Most polymer blends consist of thermodynamically immiscible components. The resulting multi-phase morphology has a considerable influence on the mechanical properties of the blend [1–3]. It is well known that the morphology of a heterogeneous polymer system is influenced by the properties of the blend components, e.g. rheological and interfacial properties [4–6], the blend composition, and by the preparation conditions [7].

During melt mixing of immiscible viscoelastic polymer melts the development of the morphology is governed by both the mechanisms of drop deformation to fibres and their break-up resulting in smaller structures, and by coalescence which leads to coarsening [8]. Within the factors influencing both processes, the interfacial tension $\gamma_{1,2}$ between the blend components plays a major role. At smaller interfacial tension between the two blend components finer dispersion due to the drop deformation and break-up mechanism can be achieved. In addition, reduced interfacial tension results in a decrease in the tendency of coarsening due to coalescence. Other factors, which are related to the interfacial tension by thermodynamic models, include the interfacial thickness, the Flory–Huggins interaction parameter, or the work of adhesion.

With this in mind, it is understandable that in recent years the number of publications dealing with the determination of interfacial tension of polymer melts is increasing rapidly. New methods, such as fibre retraction [9,10] and retraction of ellipsoidal drops [11] have been developed. Established methods, especially drop profile methods (pendant drop, spinning drop, bubble pressure method) that have been commonly used to study low molecular weight fluids, are now being applied to viscous polymer melts at elevated temperatures [12]. The capillary break-up method based on Tomotika's theory [13,14] was also applied to measure the interfacial tension of polymer blends [15,16] and is now widely used. In addition, it is possible to calculate interfacial tension from the surface tension γ of the single components if the polarities of the materials are known [12].

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* Corresponding author. Tel.: +49-351-4658-395; fax: +49-351-4658-565.

E-mail address: poe@ipfdd.de (P. Pötschke).

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Nevertheless, the measurement of both surface tension and interfacial tension between polymer melts is possible only by the drop methods.

The pendant drop analysis (PDA) is a powerful tool for determining surface and interfacial tension of polymer melts. However, there are some limitations to apply PDA to polymers. PDA requires an equilibrium state of the melt droplet. Due to the high viscosity of polymer melts, high temperatures and long annealing times are necessary to achieve equilibrium. Therefore, thermally instable materials cannot be studied by PDA. Heterogeneous structures can also cause problems because phase separation can occur. In this case, the measured value does not give the surface tension of the whole material, but it is governed by the material at the surface of the droplet.

One goal of our studies is to clarify the influence of surface properties of the molten blend components on the morphology of thermoplastic polyurethane (TPU) blends with polyolefins (PO) which were melt mixed in a twin screw extruder [3]. By proper compatibilisation this inherently incompatible blend system gives the opportunity to reduce density and price as well as to enhance processing behaviour and chemical and hydrolytic resistance as compared to TPU. In addition, surface properties, e.g. paintability or haptics, of non-polar polyolefins can be improved by mixing them with polar TPU. In this context, TPU/PO blends based on polyether TPU are compared with blends based on polyester TPU. TPUs are block copolymers consisting of hard segments (HS) and soft segments (SS). They contain a large amount of thermal labile urethane bonds, which hinders the determination of surface or interfacial tension above the TPU melting temperature. Therefore, we used model substances for the SS and the HS. In this paper (Part I), the measurements of the surface tensions of model substances for TPU are presented as well as surface tensions of polyethylene (PE) and polypropylene (PP). Part II will present interfacial tension phenomena between the model substances for the TPU segments and polyolefins and relates these findings to the morphology of TPU/PE blends.

2. Experimental

2.1. Materials and characterisation

For our work we used two types of TPU (Fig. 1) with the same HS based on 4,4′-methylenebisphenyldiisocyanate (MDI) and 1,4-butanediol (BD). The SS of the TPUs consist of polyetherdiol (PEt-diol, based on polytetrahydrofuran (PTHF)) or polyesterdiol (PEs-diol, based on adipinic acid and aliphatic diols). The polydiols are chain extended and coupled to the HS by MDI. The materials used are commercially available from Elastogran GmbH (PEs–TPU = Elastollan® C64D, PEt–TPU = Elastollan® 1195A).

As model compounds for the TPU SS we used PEt-diol ($M_n = 1000$ g/mol) and PEs-diol ($M_n = 2000$ g/mol), both commercially used for the preparation of TPUs. To hide the strong influence of the hydroxylic end groups on the surface properties, the materials were either acetylated or chain extended by MDI. To analyse the differences between both end group modification methods in case of PEt-diols, we studied in addition PEt-diols with $M_n = 650$ and 2000 g/mol.

Two types of TPU HS models have been studied, one highly crystalline based on MDI and BD [17] as used in commercial TPUs and an amorphous HS based on BD and a mixture of 2,4′- and 2,2′-methylenebisphenyldiisocyanate (2,4′-MDI and 2,2′-MDI). All model substances were provided by BASF AG. Their structures are shown in Fig. 2.

The polyethylene used in the blends with TPU was a high density PE commercially available from BASF AG (Lupolen® 4261A). A PE with low viscosity (Mirathen A 17 MA, Leuna AG) and a PP (PPXAV 10AFOB, Hoechst AG) were used for the measurements of the surface tension.

2.2. Pendant drop analysis

The surface and interfacial energy data were obtained by means of a pendant drop apparatus. This self-made apparatus (Institute of Polymer Research Dresden, Germany) consists of a NRL contact angle goniometer (Rame-Hart Inc.) equipped with an optical bench, illuminator and microscope, environmental chamber with

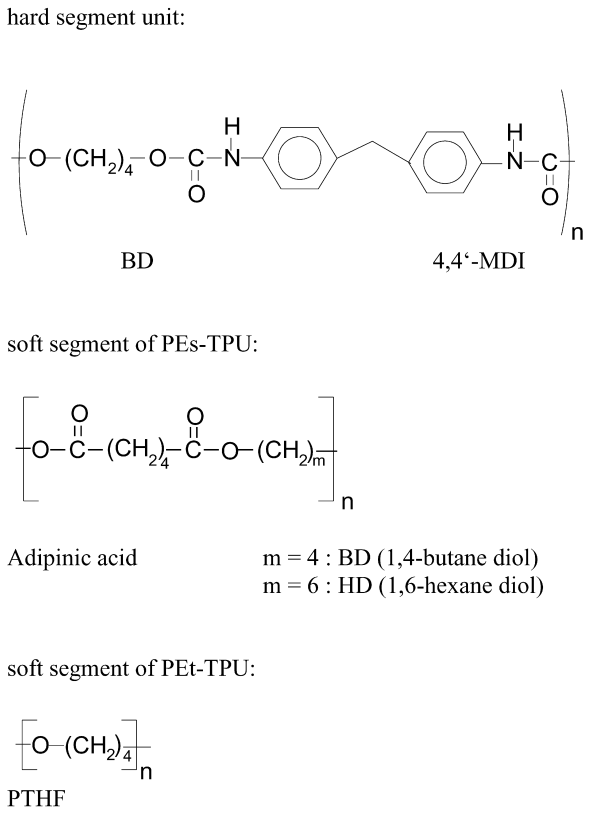

Fig. 1. Chemical structure of TPU.

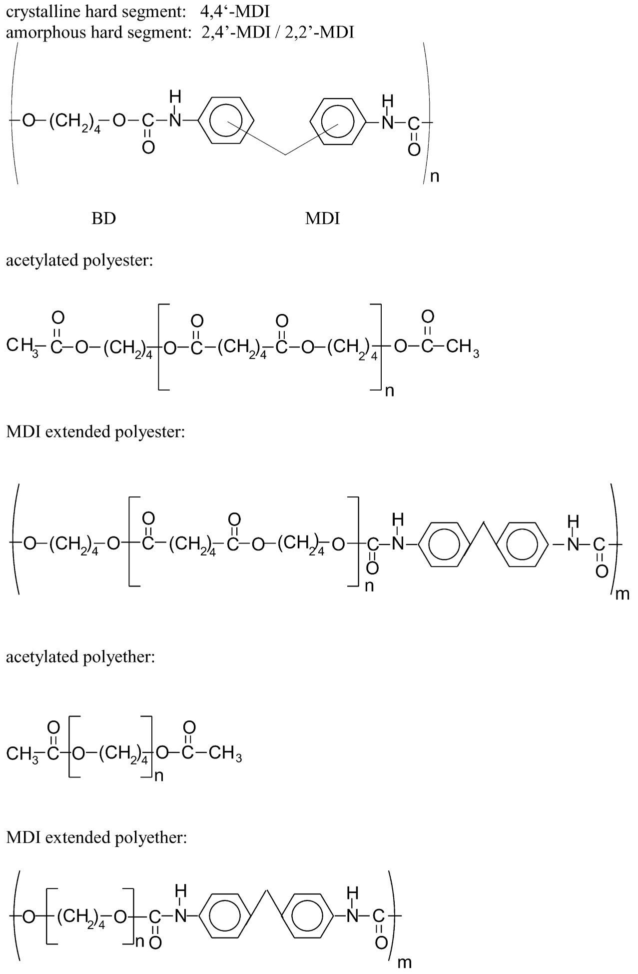

Fig. 2. Chemical structure of TPU model compounds used for PDA measurements.

temperature controller, a heatable syringe attachment, a video camera (Sony XC 77 CE), and a RGB monitor (Sony PVM 1442 QM). The experimental set-up is shown in Fig. 3.

A weak argon flow is conducted through the environmental chamber. The temperature in the chamber and of the syringe can be controlled within 1 K in a temperature range from room temperature to 344 °C. The apparatus is controlled by a personal computer, equipped with a frame grabber, image analysis software (BioScan Optimas V 3.01), and a drop shape analysis software (DSA, Krüss, Germany) based on the algorithm developed by Song and Springer [19]. The drops were formed at the tip of the syringe by pressing material out of the syringe by means of a set screw. The time to achieve equilibrium was between 10 and 30 min and was controlled by a timed fitting of the digitised drop profiles.

The drop shape analysis was performed in three steps. First, the drop images has to be digitised; from this drop image a binary drop profile is extracted; finally, a curve fitting program compares the experimental drop profile with theoretically calculated profiles according to the Laplace equation (e.g. Ref. [12] and references given therein):

$$\Delta p = \gamma_{1,2}(1/R_1 + 1/R_2) \tag{1}$$

The Laplace equation links the difference in pressure Δp at the curved interface to the interfacial tension $\gamma_{1,2}$ (in case of a liquid–vapour interface we consider the interfacial tension $\gamma_{1,2}$ as surface tension γ of the liquid). The values of R_1 and R_2 are the principal radii of curvature of the interface. The interfacial tension is linear dependent on the density difference between the

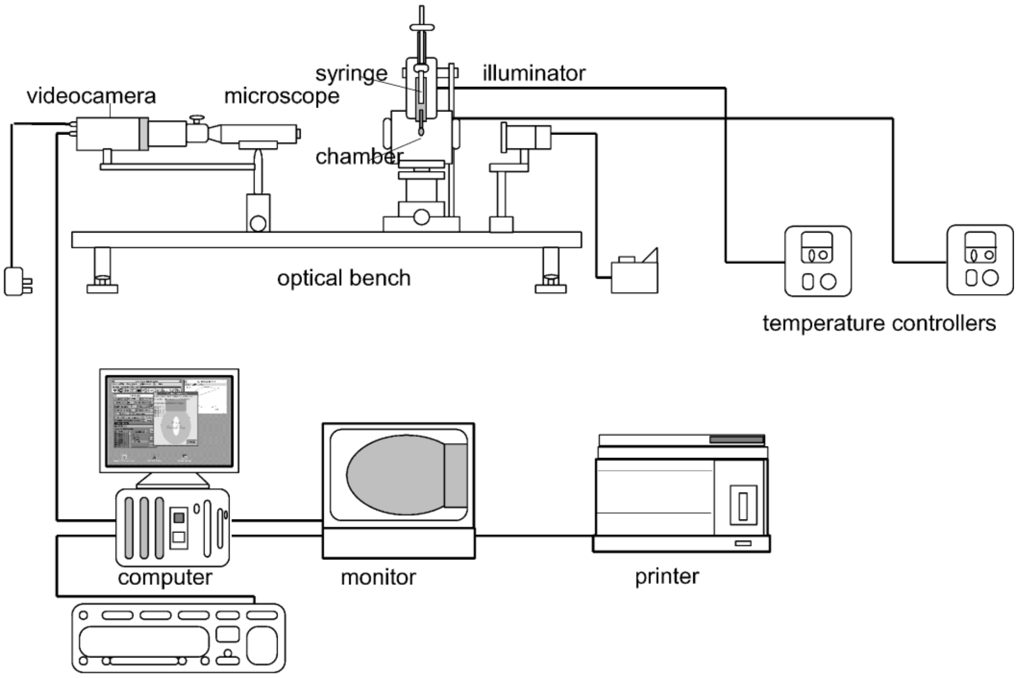

Fig. 3. Experimental set-up for the pendant drop method.

Table 1
Density data of TPU model substances and polyolefins

Material	Results PVT measurements			Density ρ at ambient conditions	
Notation	Linear regression density ρ (g/cm^3) $= A - B \times T$ (°C)		T range (°C)	ρ (g/cm^3)	T (°C)
	A (g/cm^3)	B (g/cm^3 °C)			
TPU-HS	1.2736	0.000696	113–174	1.238	25
PEt-diol 650 g/mol acetylated	1.0129	0.000736	25–90	0.994	25[a]
	1.0132	0.000733	90–172		
PEt-diol 1000 g/mol acetylated	1.0060	0.000687	41–100	0.986	32[a]
	1.0069	0.000695	100–196		
PEt-diol 2000 g/mol acetylated	1.0004	0.000687	60–172	1.040	25
PEt-diol 650 g/mol MDI extended	1.1070	0.000708	137–198	1.086	25
PEt-diol 1000 g/mol MDI extended	1.0875	0.000686	100–217	1.051	25
PEt-diol 2000 g/mol MDI extended	1.0394	0.000669	136–196	1.057	25
PEs-diol 2000 g/mol acetylated	1.1327	0.000750	47–199	1.109	32[a]
PEs-diol 2000 g/mol MDI extended	1.1694	0.000719	41–192	1.175	25
PP XAV 10A FOB	0.8558	0.000550	166–240	0.891	25
PE 17 MA	0.8664	0.000561	133–288	0.913	25

[a] Determined as liquid in a calibrated 25 cm^3 pycnometer.

pendant drop and the surrounding medium. Therefore, an accurate knowledge of the density data at the measuring temperature is necessary.

For each temperature, between three and five drops were formed and analysed. The reproducibility of the surface tension measurements was within ±0.2 mN/m.

2.3. Determination of density data

Densities ρ of solids at 25 °C were determined with an Ultrapycnometer 100 (Quantochrome) equipped with a 50 cm^3 pycnometer cell. Helium was used as the test gas. The densities of the liquid model substances were determined at 25 or 32 °C by a calibrated 25 cm^3 pycnometer. The dependence of the density on temperature was calculated from the PVT data by means of a GNOMIX PVT Apparatus (Gnomix, USA). PVT data were obtained in isothermal standard mode (ITS) by raising temperature in steps of 15 K starting from room temperature and covering at least the temperature range of the PDA measurements. The pressure was raised from 10 to 200 MPa in steps of 10 MPa. The specific volume at atmospheric pressure was extrapolated by the data obtained between 10 and 30 MPa in steps of 1 MPa according to the Tait equation [20] for each temperature by the GNOMIX PVT software. The dependency of the density on the temperature was fitted linearly in the temperature ranges used for PDA measurements (Table 1). The accuracy of the specific volume data is ±0.002 cm^3/g.

3. Results

3.1. Surface tensions of TPU model substances

Any attempts to determine the surface tension of the TPU block copolymers failed since no stable droplet could be formed. It is known that TPUs are thermally instable due to the reversibility of the polyreaction resulting in the urethane group. The opening of the urethane bond occurs starting at 160 °C while the melting range of the HS extends to 240 °C [17,18]. Therefore, we studied the different segments of TPU. As SS we used PEt-diol with $M_n = 1000$ g/mol and PEs-diol with $M_n = 2000$ g/mol.

The HS used in the commercial TPUs was also not measurable by PDA because of its crystallinity. At temperatures above the melting point, thermal depolymerisation and side reactions occurred. Thus, we used the amorphous model HS. The amorphous and the crystalline HS are isomeric polymers consisting of the same structural units. The only difference is that the amorphous HS contains partially *ortho*-isomeric structures (which hinder its crystallisation) while the crystalline HS has a fully *para*-isomeric structure. Furthermore, during melt mixing the crystalline HS is also present in an amorphous state. Therefore, the amorphous HS is an acceptable substitute for the crystalline HS in our studies. The temperature range in which a stable drop of it could be formed was 120–165 °C. For the model SS measurements could be carried out for both end group modifications. The acetylated PEs-diol was measurable between 55 and 100 °C, and its MDI extended version between 175 and 195 °C. The temperature range for the acetylated PEt-diol was 23–180 °C and for the MDI extended form the melt was analysed at 160 and 190 °C.

Table 2
Results of surface tension measurements of TPU model substances and polyolefins using PDA

Notation	T (PDA) (°C)	ρ (g/cm^3)	γ (mN/m)	Linear regression surface tension $\gamma\,(\mathrm{mN/m}) = A - B \times T$ (°C)		γ at 175°C extrapolated (mN/m)
				A (mN/m)	B (mN/m °C)	
TPU-HS	120	1.1901	47.8	55.4	0.0638	44.2
	140	1.1762	46.2			
	150	1.1692	45.8			
	165	1.1588	44.9			
PEs-diol 2000 g/mol acetylated	57	1.0899	41.6	46.6	0.0880	31.2
	80	1.0727	39.7			
	100	1.0577	37.8			
PEs-diol 2000 g/mol MDI extended	175	1.0436	31.7	41.4	0.0552	31.7
	180	1.0400	31.4			
	185	1.0364	31.2			
	190	1.0328	30.9			
	195	1.0293	30.5			
Both PEs-diols together				46.0	0.0805	32.0
PEt-diol 650 g/mol acetylated	23	0.9960	39.3	41.4	0.0944	24.9
	60	0.9688	35.5			
	100	0.9399	31.9			
	140	0.9106	27.8			
	180	0.8813	24.8			
PEt-diol 1000 g/mol acetylated	23	0.9904	37.8	39.5	0.0822	25.1
	60	0.9648	34.7			
	100	0.9373	31.0			
	140	0.9096	27.6			
	180	0.8818	25.1			
PEt-diol 2000 g/mol acetylated	60	0.9592	35.2	39.8	0.0776 T	26.2
	100	0.9317	31.8			
	140	0.9042	28.9			
	180	0.8767	25.8			
PEt-diol 650 g/mol MDI extended	145	1.0043	32.4	36.7	0.0295 T	31.5
	160	0.9937	31.9			
	175	0.9831	31.5			
	190	0.9725	31.1			
PEt-diol 1000 g/mol MDI extended	160	0.9778	32.0	40.8	0.0553	31.2
	190	0.9572	30.3			
PEt-diol 2000 g/mol MDI extended	165	0.9292	29.5	40.1	0.0638	28.9
	175	0.9675	29.0			
	185	0.9606	28.3			
	190	0.9572	27.9			
PP XAV 10A FOB	160	0.7677	22.0	30.7	0.0538	21.3
	185	0.7540	20.9			
	210	0.7402	19.6			
	220	0.7347	18.8			
	235	0.7265	18.0			
PE 17 MA	162	0.7751	26.8	33.1	0.0390	26.3
	182	0.7643	26.1			
	202	0.7531	25.2			
	222	0.7418	24.5			

Fig. 4 shows digitised drop shapes of the acetylated PEt-diol and PEs-diol at 100 °C and of the amorphous TPU-HS at 120 °C. The shapes exhibit differences in the ratio between the principal radii of curvature. From the shape analysis without considering the differences in the densities of the drops you can obtain values of the surface tension divided by the density, which are shown in Fig. 4. These values, reflecting only the different drop shapes, differ less from each other than the real surface tension data (compare to Table 2), which are a product of shape factors and the real density. Therefore, the PDA results sometimes in rather different values even if the drop shapes of the liquids are very similar. In our systems the density of HS is higher, while for the PEt model compounds, it is lower (Table 2).

The obtained values of the surface tension are shown in Table 2 and Fig. 5. The highest surface tension, values between 50 and 46 mN/m, was observed for the amorphous HS. Although it is expected that TPU-HS has a high surface

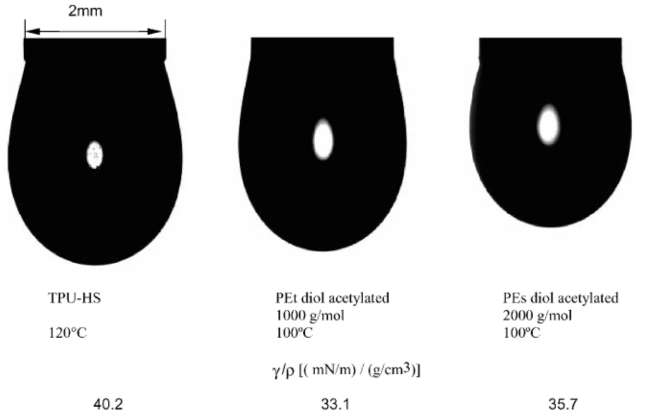

Fig. 4. Digitised drop shapes as measured by PDA.

tension, we have not found any value for the molten state in literature. The very high values compared to SS explain the fast and strong phase segregation in the TPU multi-block copolymers.

The surface tension of the acetylated PEs-diol is significantly higher than that of PEt-diol. Acetylated and MDI extended PEs-diol follow the same temperature dependency and can be described by a single linear fit. The values for the acetylated PEt-diol are about 5 mN/m lower than that of the acetylated PEs-diol. But the MDI extended version of the PEt-diol shows higher surface tensions than the acetylated ones, comparable to the surface tensions of MDI extended PEs-diol. Although the differences in polarity and surface tension between PEt-diol and PEs-diol based SS are expected qualitatively and explainable by their chemical structures, no values for the molten state are given in the literature. The linear fits of the surface tension dependencies on temperature are given in Table 2 and were used to extrapolate the values to an uniform temperature of 175 °C.

3.2. Surface tension of polyolefins

The PE material used in the blends (Lupolen® 4261A) was not measurable by PDA because of its high viscosity and high elasticity. The surface tension of Mirathen A17 MA could be measured between 162 and 222 °C. The lower viscous PP was measurable between 160 and 235 °C.

The surface tension of the PP is lower than that of the PE. The difference between both polymers is about 5 mN/m. This is in accordance with values given by Wu [12, p. 89] and Roe [21]. Also, the quantitative values match very well with the data given in the literature [12,21].

At 175 °C the PP has the lowest surface tension (21.3 mN/m) compared to all other components. Polyethylene shows lower values (26.2 mN/m at 175 °C) compared to both MDI extended SS and the TPU HS (Fig. 5).

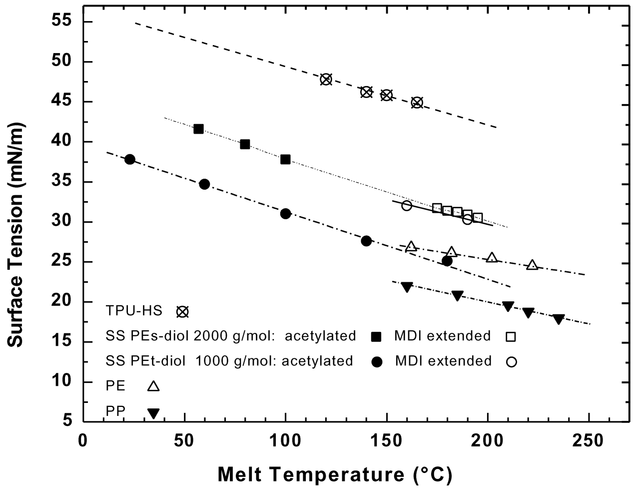

Fig. 5. Surface tension of model substances for the TPU hard segments (HS), soft segments (SS) and polyolefins.

3.3. Comparison of surface tension values for TPU model substances and polyolefins

The decrease of the surface tension with melt temperature is about the same for the HS and the SS in the acetylated form. The MDI extended samples show a lower temperature coefficient, but the suitable temperature ranges for PDA studies were much smaller. The polyethylene shows a temperature coefficient of 0.039 that is lower than temperature coefficient described by Wu (0.057 in Ref. [22]), Roe (0.058 in Ref. [21]), and Song and Springer (0.069 in Ref. [19]) for LDPE. The polypropylene surface tension has a temperature coefficient of 0.054, which is in good agreement with values given by Roe (0.056 in Ref. [21]), Everaert et al. (0.054 in Ref. [23]) and values summarized by Wu (0.058, 0.040 in Ref. [12]).

The differences between the surface tensions at a given temperature are very significant. Using 175 °C as reference temperature and extrapolating the measured values, the highest difference is that between TPU-HS and PP or PE with 22.9 or 17.9 mN/m, respectively. The difference between the surface tensions of PP and PEt-diol is 3.8 mN/m in its acetylated form and 9.9 mN/m for the MDI extended form. The differences between the surface tension values of PP and the PEs-diols are 10.7 mN/m. Polyethylene shows differences in its surface tension to the PEs-diols of 5.7 mN/m, its surface tension is 4.9 mN/m lower than that of MDI extended PEt-diol, but 1.2 mN/m higher as that of the acetylated PEt-diol. Here, possibly the low molecular weight of the PEt-diol leading to low surface tension is dominating over the effect of the more polar structure elements (see below). Because of the much lower differences in surface tension of the polyolefins to the SS as compared to the HS we can suppose that at the interface to the polyolefinic component in blends of TPU with PO favourably TPU SS are located. This will be discussed more intensively in Part II.

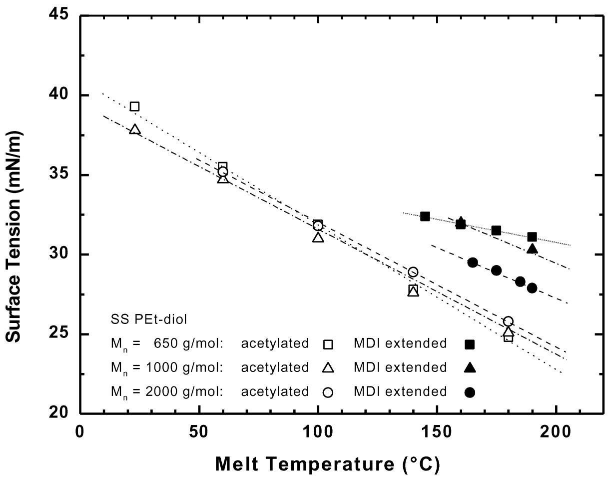

Fig. 6. Surface tension of model substances for the TPU soft segments, based on PTHF at different molecular weights.

3.4. Influence of molecular weight and the end group modification on the surface tension of PEt based model soft segments

The strong dependence of the surface tension of PEt-diol on the end group modification encouraged us to look in detail into these differences. Therefore, it was also meaningful to study the molecular weight influence.

Fig. 6 shows the dependence of surface tension on temperature for three different molecular weights of the PEt-diol samples as well as in the acetylated as in the MDI extended form. The surface tension of the acetylated PEt-diols is nearly independent of the molecular weight. In comparison, all MDI extended samples exhibit higher values of surface tension, but the difference diminishes with increasing molecular weight of the PEt segments. At $M_{\text{n}} = 2000$ g/mol the difference between the acetylated and the MDI extended sample is only 2.7 mN/m; at $M_{\text{n}} = 650$ g/mol the difference is 7.6 mN/m at 190 °C and 4.7 mN/m at 145 °C.

The dependency of the surface tension on the molecular weight is caused by the different contents of MDI chain extender which form the high polar urethane segments. In the chain extended diol with $M_{\text{n}} = 650$ g/mol the MDI content is 27.8 wt% while in the diols with $M_{\text{n}} = 2000$ g/mol only 11.1 wt% MDI are present. For comparison, the MDI content in the HS is 73.5 wt%.

In PEs-diols the influence of the kind of chain end modification is less pronounced since the PEs segments exhibit intrinsically a higher surface tension value because of its more polar character. The MDI based urethane units are not dominating its surface tension.

4. Summary and conclusions

The method of PDA is a useful tool for the determination of surface tensions of viscoelastic polymers at elevated temperatures, but it cannot be applied to thermal labile multi-phase systems like TPUs. However, when selecting proper model compounds information about the surface properties of the thermal labile phase segregated block copolymers can be obtained.

Surface tensions of the different segments of TPU were measured in the melt for the first time. As model compounds for the SS, a polyetherdiol (PEt-diol) and a polyesterdiol (PEs-diol) were used. To reduce the influence of the hydroxyl end groups on the surface properties, the diols were either acetylated or chain extended with MDI. The influence of the molecular weight and the end group modification on the surface tension was investigated for the PEt-diol. An amorphous HS model was synthesised to investigate the surface tension of the HS units. It could be shown that the surface tension of the HS is significantly higher than that of the SS. The amorphous HS shows surface tensions between 50 and 46 mN/m at 120–165 °C, which is a very high value compared to common polymers [12]. The surface tension of PEs-diols was found higher than that of PEt-diol model substances. For PEt-diol a difference was found between the values of acetylated and MDI extended samples, which reduces with increasing molecular weight of the PEt segments. In PEt-diol the highly polar MDI based urethane groups have a more significant influence on the surface tension than in the PEs-diol system, which exhibits a higher intrinsic surface tension.

Polyolefins show lower surface tensions than the TPU hard segment and MDI extended SS model substances. Surprisingly, acetylated PEt-diols have very low surface energies even lower than PE possibly due to the dominating influence of the low molecular weight.

Due to the higher differences between the surface tensions of the hard and SS, we can conclude that the phase segregation is stronger and faster in TPUs based on PEs SS than in PEt–TPU. In blends with polyolefins we can suppose that the SS (and not the HS) will be enriched at the interface and therefore determine the interfacial tension between TPU and polyolefins because of the more similar surface tensions of SS and PO compared to them of HS and PO. In addition, we can conclude that under otherwise comparable conditions blends of PO with TPU based on PEs-diol will have coarser morphologies than those with TPU based on PEt-diol because of the higher differences in surface tensions between PEs SS and PO than between PEt SS and PO. These aspects will be discussed in more detail in Part II.

References

[1] Schmitt BJ. Angew Chem 1979;91:286–309.
[2] Wu S. Polymer 1985;26:1855–63.
[3] Pötschke P, Wallheinke K, Fritsche H, Stutz H. J Appl Polym Sci 1997;64:749–62.
[4] Favis BD, Chalifoux JP. Polym Engng Sci 1987;27(20):1591–9.

[5] Hietaoja PT, Holsti-Miettinen RM, Seppälä JV, Ikkala OT. J Appl Polym Sci 1994;54:1613–23.

[6] Wu S. Polym Engng Sci 1987;27(5):335–43.

[7] Utracki LA, Shi ZH. Polym Engng Sci 1992;32(24):1824–33.

[8] Sundararaj U, Macosko CW. Macromolecules 1995;28:2647–57.

[9] Carriere CJ, Cohen A, Arends CB. J Rheol 1989;33(5):681–9.

[10] Cohen A, Carriere CJ. Rheol Acta 1989;28:223.

[11] Luciani A, Champagne MF, Utracki LA. J Polym Sci, Part B: Polym Phys 1997;35:1393–403.

[12] Wu S. Polymer interface and adhesion. New York: Marcel Dekker; 1982.

[13] Tomotika S. Proc R Soc Lond, Ser A 1935;150:322–37.

[14] Tomotika S. Proc R Soc Lond, Ser A 1936;153:302–18.

[15] Chappelear DC. Polym Prepr 1964;5:363–4.

[16] Elemans PHM, Janssen JMH, Meijer HEH. J Rheol 1990;34(8): 1311–26.

[17] Pompe G, Pohlers A, Pötschke P, Pionteck J. Polymer 1998;39(21): 5147–53.

[18] Allport DC, Mohajer AA. Property–structure relationships in polyurethane block copolymers. In: Allport DC, Janes WH, editors. Block copolymers. New York: Wiley; 1973. p. 443–92. Chapter 8C.

[19] Song B, Springer J. J Colloid Interf Sci 1996;184:64–91.

[20] Rodgers PA. J Appl Polym Sci 1993;484:1061–80.

[21] Roe RJ. J Phys Chem 1968;72(6):2013–7.

[22] Wu S. J Colloid Interf Sci 1969;31(2):153–61.

[23] Everaert V, Groeninckx G, Pionteck J, Favis BD, Aerts L, Moldenaers P, Mewis J. Polymer 2000;41(3):1011–25.