WOJCIECH PISULA[1], JACEK PIGŁOWSKI[2)*], CLAUDIA KUMMERLÖWE[3]

Preparation and characterization of copolyesters of poly(tetramethylene succinate) and poly(butylene terephthalate)

Summary — Polymer blends of poly(tetramethylene succinate) (PTMS), a biodegradable aliphatic polyester, and poly(butylene terephthalate) (PBT), a non-biodegradable polyester with aromatic elements, were prepared by melt mixing. Transesterification reactions between both polyesters were promoted by the addition of zinc acetate as a catalyst. The transesterification reaction was evaluated by FT-IR measurements combined with solubility tests and ^{1}H NMR spectroscopy. The molecular structure of the copolyesters is influenced by the catalyst content and the initial blend composition. Thermal and mechanical properties and the morphology of the resulting material were characterized.

Key words: polymer blends, reactive processing, transesterification, poly(tetramethylene succinate), poly(butylene terephthalate).

OTRZYMYWANIE I CHARAKTERYSTYKA KOPOLIESTRÓW Z POLI(BURSZTYNIANU BUTYLENOWEGO) I POLI(TEREFTALANU BUTYLENOWEGO)

Streszczenie — Na drodze mieszania stopionych poliestrów: poli(bursztynianu butylenowego) (PTMS) i poli(tereftalanu butylenowego) (PBT) uzyskano mieszaniny o różnym składzie ilościowym. Obydwa polietery różnią się zasadniczo właściwościami. PTMS jest polimerem biodegradowalnym, podczas gdy PBT mimo podobieństwa w budowie, ze względu na obecność aromatycznego pierścienia w łańcuchu głównym, nie wykazuje tej cechy. W przypadku prostego mieszania uzyskuje się niejednordną mieszaninę, którą łatwo rozdzielić wykorzystując różnice w rozpuszczalności. Dodatek octanu cynku sprzyja reakcji transestryfikacji i uzyskaniu kopoliestru. Strukturę kopoliestru badano za pomocą FT-IR (rys. 1 i 2, tabela 2) oraz ^{1}H NMR (rys. 3 i 4). Struktura mieszaniny silnie zależy od składu kompozycji (rys. 5 i 6). Przykładowo krystaliczność PBT w mieszaninie PBT/PTMS 80/20 otrzymanej w obecności katalizatora niewiele się zmienia i praktycznie zanika w mieszaninie PBT/PTMS 20/80. W pracy zamieszczono również właściwości termiczne (rys. 9 i 10, tabela 3), mechaniczne (rys. 14, tabela 4) oraz obrazy morfologii badanych mieszanin (rys. 11—13).

Słowa kluczowe: mieszanki polimerowe, przetwórstwo reaktywne, reakcja transestryfikacji, poli(bursztynian butylenowy), poli(tereftalan butylenowy).

During the last years plastic waste management became a topic of public and scientific discussion as well. It is obvious that the environmental problems can only be solved if the amount of post-consumer plastic waste in landfill areas will be drastically reduced. Application of biodegradable packaging could reduce the problem. Many aliphatic polyesters are biodegradable thermoplastic materials and received therefore much attention as candidates for biodegradable films, fibres, bottles, and injection molded products [1—4]. The drawbacks of these materials are their poor mechanical performance and the narrow processing windows. Therefore several attempts have been published to improve the properties of the biodegradable polyesters by blending with other polymers [5—7] or by copolymer formation [8—13]. Polyesters containing aromatic sequences are commercially used as packaging materials due to their favourable mechanical properties, however, polyesters with aromatic sequences are resistant to biological attack [8, 12, 14].

In this study, we report on transesterification reactions of poly(tetramethylene succinate) (PTMS) and poly(butylene terephthalate) (PBT) and the resulting properties of the copolymers. PTMS is an aliphatic polyester that can be synthesised from 1,4-butanediol and succinic anhydride [15]. PTMS is a highly crystalline [16—19] material and exhibits an equilibrium melting temperature of 129 °C [20]. Glass transition temperatures between -40 °C [16, 21] and -27 °C [20] were reported. The high crystallinity of PTMS retards biodegradation and results in unfavourable mechanical properties.

Poly(tetramethylene succinate/terephthalate) copolymers synthesised from succinic acid, dimethyl terephthalate and butanediol exhibit an enhanced biodegra-

---

[1] Max-Planck Institute for Polymer Research Mainz, Department of Polymer Physics, Ackermannweg 10, D-55128 Mainz, Germany.

[2] Wrocław University of Technology, Faculty of Chemistry, Polymer Engineering and Technology Group, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

[3] University of Applied Sciences Osnabruck, Faculty of Engineering and Informatic, Albrechtsstraße 30, D-49076 Osnabrück, Germany.

[*] Corresponding author.

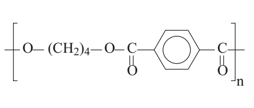
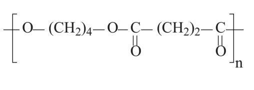
dation if they show a low crystallinity [16]. Polymer blends and copolymers of PTMS and PBT were studied earlier [6, 11]. Both polymers do not undergo transesterification reactions when they were melt blended at 240 °C [6]. However, at processing temperatures of 290 °C and sufficiently long reaction times the formation of copolymers was detected by ^{1}H NMR measurements [11]. In the present work, PTMS and PBT were subjected to reactive blending in the presence of zinc acetate as a catalyst promoting transesterification reactions. The effect of the catalyst on the molecular structures of the resulting copolymers will be evaluated by combination of FT-IR measurements, solubility studies and ^{1}H NMR spectroscopy. The polymers were produced with the aim to obtain the materials showing enhanced mechanical performance and sufficient biodegradability.

EXPERIMENTAL

Materials

PTMS and PBT were supplied by Aldrich. Intrinsic viscosity and number average molecular weights were determined by Ubbelohde viscometry in chloroform for PTMS and in tetrachloroethane/phenol 40/60 for PBT. The data are summarized in Table 1. Before use the polymers were dried in a vacuum oven at 90 °C for 24 h.

Table 1. Characteristics of the polymers

Polymer	Formula	Intrinsic viscosity dL/g	M_n kg/mol
PBT		0.90$^{*)}$	29$^{*)}$
PTMS	 $\left[O-(CH_2)_4-O-\underset{O}{\underset{\|}{C}}-(CH_2)_2-\underset{O}{\underset{\|}{C}} \right]_n$	0.71$^{**)}$	20$^{**)}$

$^{*)}$ Tetrachloroethane/phenol 40/60, 30 °C, $[\eta] = 1.166 \cdot 10^{-4} M_n^{0.871}$ [22].
$^{**)}$ Chloroform, 25 °C, $[\eta] = 2.15 \cdot 10^{-4} M_n^{0.82}$ [23].

The solvents: chloroform, tetrachloroethane, phenol, deuterated trifluoroacetic acid and the catalyst zinc acetate [$Zn(CH_3COO)_2$] were delivered by Aldrich and Merck and used as received.

Blend preparation

PBT/PTMS blends were prepared by melt blending using an internal mixer at temperature of 260 °C. The mixing time was fixed to 20 min. The mixer was rinsed with nitrogen (100 L/h) to prevent degradation of the polymers during processing. Details of the instrument and procedure are described elsewhere [24]. The mixing conditions were the same for all blends. The PBT/PTMS blend ratio varied in steps of 20 wt. %. Three different samples of each PBT/PTMS blend composition were prepared with increasing amounts of $Zn(CH_3COO)_2$ catalyst. The catalyst concentrations were 0.0, 0.1 and 0.5 parts per hundred polymer (phr). After melt blending the samples for mechanical tests were obtained by compression molding in a hydraulic press at temperature of 260 °C as described in [24].

Method of testing

Chemical characterization

The transesterification products were analysed by FT-IR and ^{1}H NMR spectroscopy. For FT-IR studies a Nicolet 320 spectrometer (32 scans, resolution 4 cm^{-1}) was used. Before FT-IR measurements, the PBT/PTMS samples were separated to a chloroform soluble fraction and an insoluble fraction by extraction of 0.45 g of the respective blend in 10 mL chloroform for 24 h. Solution and remaining insoluble part were separated by filtration, dried and examined as the films on KBr pellets. ^{1}H NMR analysis was carried out in a 250 MHz Bruker spectrometer. Solutions of the PBT/PTMS samples in deuterated trifluoroacetic acid were used.

Viscosity measurements

The intrinsic viscosity [η], of PBT and the inherent viscosities (η_{inh}) of PBT/PTMS blends were determined using Ubbelohde viscometer in tetrachloroethane/phenol (40/60) at 30 °C. Intrinsic and inherent viscosities are defined in the usual way:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \tag{1}$$

and

$$\eta_{inh} = (\ln \eta_{rel})/c \tag{2}$$

where: $\eta_{rel} = \eta/\eta_0$, $\eta_{sp} = \eta_{rel} - 1$, η_0 — *viscosity of the respective solvent*, η — *viscosity of the polymer solution*.

For the blends, two sets of solutions were examined: solutions of PBT/PTMS blends after melt processing and solutions of PBT/PTMS blends prepared by mixing of the granules directly in the solvent in order to prevent possible thermal degradation and to exclude transesterification reaction possible in the melt. The latter blends are called physical blends. The inherent viscosities were determined for a fixed polymer concentration of 1.055 g/dL. Chloroform as solvent and a temperature of 25 °C were used to measure the viscosities of PTMS.

Thermal properties

Thermal properties of the samples were detected by DSC measurements using a Mettler TA 3000 instrument. Fiat samples with a mass of 15—20 mg were prepared by melt pressing to ensure an optimal contact to DSC aluminum pans. All samples were exposed to the following thermal treatment: samples were heated with a rate of 20 deg/min from 25 to 260 °C, annealed at 260 °C for 3 min and then cooled with 10 deg/min to 25 °C. After this pre-treatment the samples rested for 24 h. The thermal data were finally obtained from a heating scan from -70 °C to 260 °C with a rate of 10 deg/min.

Mechanical properties

Charpy impact tests were carried out on notched samples with a size of 85 × 6 × 4 mm using a free-running pendulum with a maximum energy of 1 J. The TIRAtest 2705 machine was used for tensile tests. The crosshead speed was 1 mm/min for determination of Young's modulus and 10 mm/min for tensile strength evaluation. The sample geometry for tensile tests was 46 × 10 × 1 mm.

Morphology

Polarizing microscopy studies were performed to observe the morphology and crystallization behavior of the blends. A Zeiss Axiophot light microscope equipped with a ColorView12 camera and a Linkam THMS 600 hot stage were used. The samples, sandwiched between two cover glasses, were heated from 25 to 260 °C at a heating rate of 5 deg/min and then cooled with 5 deg/min back to 25 °C.

RESULTS AND DISCUSSION

FT-IR measurements

FT-IR spectra of pure PBT and PTMS agree completely with reference spectra [21, 25]. The bands of interest for the present study are the benzene ring vibration band of PBT at 727 cm^{-1}, the carbonyl stretching bands and the bands of the ester group either linked to an aromatic ring or to an aliphatic entity. Those bands are summarized in Table 2. The carbonyl stretching bands of both polymers appear at almost the same wave numbers and are therefore not suitable for evaluation of changes in the macromolecular structure due to transesterification reactions. Two strong bands related to C-O stretching can be seen for both polyesters. They are situated at 1271 and 1105 cm^{-1} for the ester group of PBT and at 1158 and 1046 cm^{-1} for PTMS.

Table 2. Characteristic FT-IR peaks of PBT and PTMS

FT-IR peak	Wave number, cm^{-1}	Description
	PBT	
a	1712	C=O stretching
b	1271	C–O valence
c	1105	
d	727	benzene ring vibration
	PTMS	
e	1732, 1722, 1715	C=O stretching
f	1158	C–O valence
g	1046	

To analyse the PBT/PTMS blends and to monitor transesterification reactions during the blend processing the following method was developed. PTMS is completely soluble in chloroform, whereas PBT is insoluble. The blends can be separated to a soluble and an insoluble fractions by chloroform extraction. Both fractions were then examined by FT-IR spectroscopy. Figure 1 shows as example the spectra of the PBT/PTMS 20/80 blend. Curves 1 in Fig. 1 show the spectra of the soluble and insoluble fractions of PBT/PTMS 20/80 blend prepared without catalyst. It turns out that the spectrum of the soluble fraction corresponds to PTMS since it exhibits the characteristic ester group bands of PTMS whereas that of the insoluble fraction belongs to PBT indicated by the ester group bands of PBT and the benzene ring vibration band. Processing of the same blend with zinc acetate catalyst yields completely soluble samples (curves 2 and 3). Furthermore, it can be seen that the spectra of the soluble polymer also contain the characteristic bands of the PBT ester group and the band of the benzene ring vibration. It can be concluded that the catalyst promoted a transesterification reaction leading to a soluble polymer composed of PTMS and PBT units.

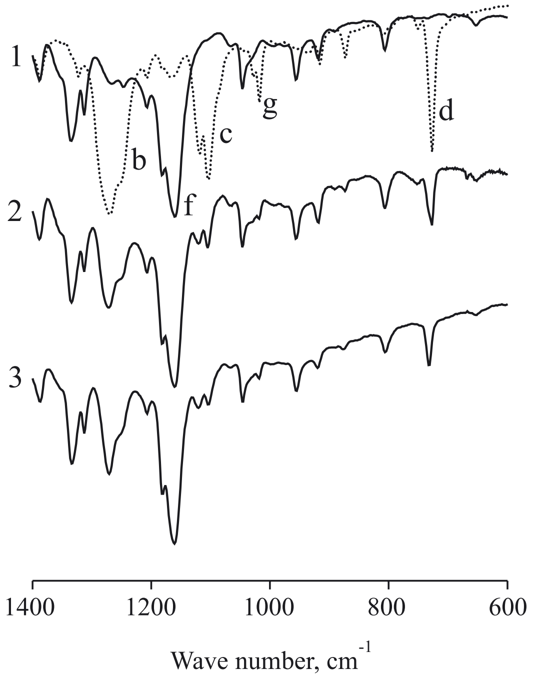


Fig. 1. FT-IR spectra of PBT/PTMS 20/80 blends obtained in reaction: 1 — without catalyst, 2 — with 0.1 phr of catalyst, 3 — with 0.5 phr of catalyst; solid lines — chloroform soluble fraction, dotted line — chloroform insoluble fraction

For a fixed blend composition the total amount of soluble fraction is rising with increasing catalyst content indicating that not only the soluble PTMS is dissolved. All blends with PTMS excess and 0.5 pph zinc acetate are completely soluble. Increasing PBT content in the blends leads to an increasing fraction of insoluble polymer. This

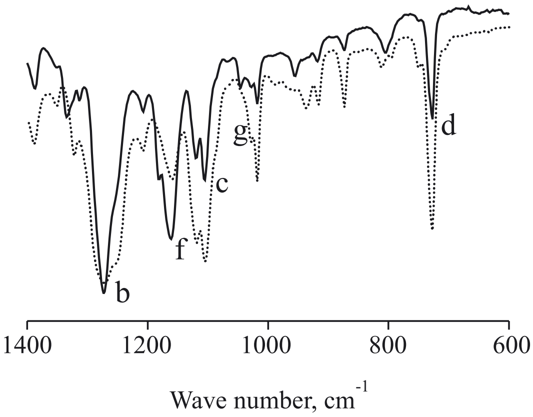


Fig. 2. FT-IR of PBT/PTMS 80/20 blend prepared with 0.5 phr catalyst; solid line — chloroform soluble fraction, dotted line — chloroform insoluble fraction

can be demonstrated in Figure 2. The chloroform extraction of the PBT/PTMS 80/20 blend processed with 0.5 phr catalyst leads to a soluble and insoluble fractions. Spectra of both fractions exhibit the characteristic peaks of PBT and PTMS. It means both fractions include the copolymers containing aliphatic and aromatic units.

The combination of solubility tests and FT-IR spectroscopy turned out to be an adequate method to characterize the changes in the macromolecular structure by interchange reactions. It can be demonstrated that during melt processing of PBT and PTMS without catalyst no exchange reactions occur whereas the presence of a catalyst yields to a formation of copolymers consisting of both aromatic and aliphatic units.

^{1}H NMR measurements

The ^{1}H NMR spectra of virgin PBT exhibit three salient signals. The protons of the tetramethylene units result in peaks at 5.1 ppm and 2.6 ppm. The peak at 8.7 ppm is attributed to the protons of the aromatic ring. PTMS shows also three marked signals at 4.8 and 2.4 ppm for the methylene protons of the butylene glycolic unit and at 3.4 ppm for methylene protons of succinic acid unit. The ^{1}H NMR spectra of PTMS are in agreement with the data reported [10, 11]. The ^{1}H NMR spectra of the blends prepared without catalyst are simply composed of the signals of the two components. The transesterification reactions during the melt processing with zinc acetate catalyst may lead to four different

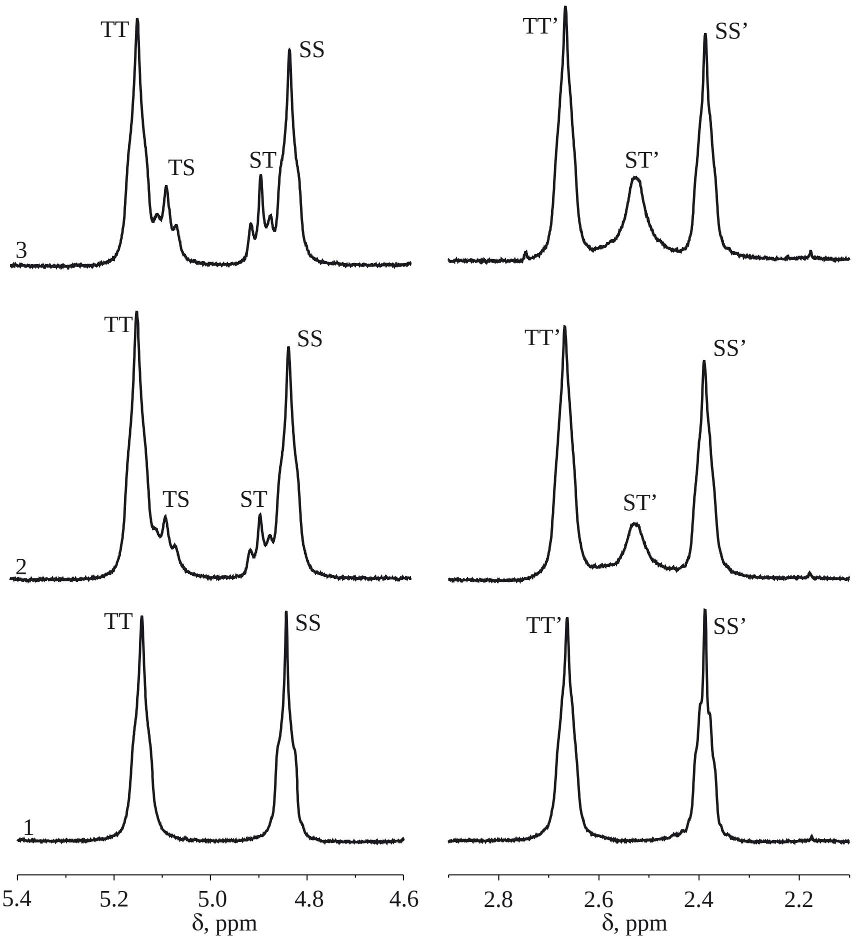
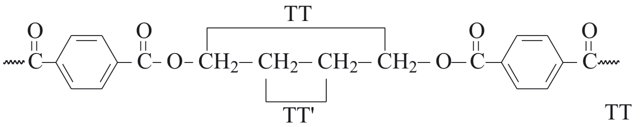
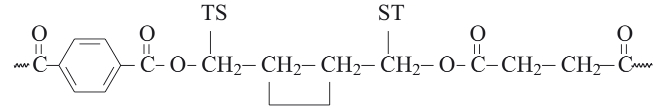


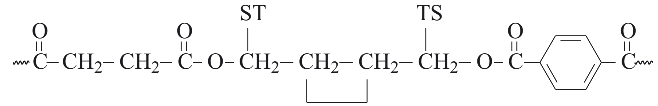
Fig. 3. Tetramethylene proton peak split in ^{1}H NMR spectra of PBT/PTMS 60/40 blends containing zinc acetate in amount: 1 — 0.0 phr, 2 — 0.2 phr, 3 — 0.5 phr



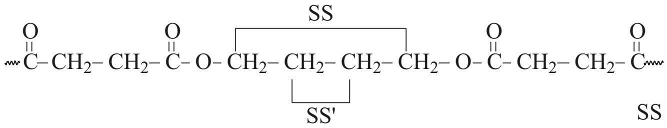
TT



TS



ST



SS

chemical environments of the tetramethylene protons as shown as formulas SS, ST, TS and TT. Besides the homopolymers, denoted as SS and TT, the copolymers having TS and ST linkages can be built up. Figure 3 shows, as an example, the ^{1}H NMR spectra of the PBT/PTMS 60/40 blend. It becomes obvious that for the blend without catalyst only the signals of protons in homopolymers or SS and TT linkages occur (Fig. 3, curve 1). With increasing catalyst content additional signals appear that can be attributed to the formation of TS and ST linkages by transesterification. The intensities of the new signals increase with increasing zinc acetate content, while the signal intensities of the homopolymers decrease. In addition, the intensities of the new peaks are noticeably higher for the blend systems PBT/PTMS 60/40 and 40/60 than for 20/80 and 80/20 blends. The ^{1}H NMR spectra reveal that by transesterification the initial homopolymer structure changes gradually at first to a block copolymer structure with relatively low amount of ST and TS linkages and finally to a random distribution of units. The macromolecular structure can be characterized by the dyad dyfractions f_{SS}, f_{TT}, f_{ST} and f_{TS} which are calculated from the relative peak areas of the respective NMR signals. The molar fraction of terephthalate (P_T) and the molar fraction of succinate (P_S) can be obtained from the relative peak areas:

$$P_T = \frac{f_{ST} + f_{TS}}{2} + f_{TT} \qquad P_S = \frac{f_{ST} + f_{TS}}{2} + f_{SS} \tag{3}$$

The determined molar fractions are in agreement with the overall molar fraction of the blend. The degree of transesterification (DT) can be calculated according to the method described in [26, 27]:

$$DT = \frac{f_{ST} + f_{TS}}{f_{TT} + f_{ST} + f_{TS} + f_{SS}} = f_{ST} + f_{TS} \tag{4}$$

The probability (P) of finding T (or S) unit next to S (or T) unit is then given by equations:

$$P_{ST} = \frac{f_{ST} + f_{TS}}{2P_S} \qquad P_{TS} = \frac{f_{ST} + f_{TS}}{2P_T} \tag{5}$$

The number average sequence length, the so-called block length (L_{ni}) of the S and T units can be calculated from

$$P_{ST} = \frac{1}{L_{nS}} \qquad P_{TS} = \frac{1}{L_{nT}} \tag{6}$$

The degree of randomness (B) is defined as the sum of the probabilities P_{ST} and P_{TS}.

$$B = P_{ST} + P_{TS} \tag{7}$$

After definitions given before, one can express the relation between P_{TS} and P_{ST} by

$$P_{TS} = \frac{P_S}{P_T} \cdot P_{ST} \tag{8}$$

Regression analysis of experimental data yields to the following relationships:

$$\begin{aligned} P_{ST} &= 1.29 \cdot (1 - P_T) \cdot P_T^{1.2} \text{ for 0.5 pph catalyst} \\ P_{ST} &= 1.33 \cdot (1 - P_T) \cdot P_T^{2} \text{ for 0.1 pph catalyst} \end{aligned} \tag{9}$$

Degree of transesterification, randomness, and block length can also be written as the functions of P_{ST}. Figure 4 and 5 present experimental data for those quantities as the functions of P_T. The solid lines are calculated using eq. (9). From Fig. 4 it can be seen that blends with balanced PBT/PTMS ratio show the highest values of DT as a consequence of the higher statistical possibility of occurrence of transesterification reactions. The number average sequence length (L_{ni}, where i is S or T) express the change in sequence distribution. $L_{ni} = 1$ corresponds to an alternating copolymer whereas $L_{ni} = \infty$ is related to a homopolymer. Sequence length decreases with increasing catalyst content for fixed blend composition (Fig. 5). The degree of randomness (B) is also indicated in Fig. 5 as a function of blend composition. A value of $B = 0$ would correspond to a homopolymer blend. A random distribution of terephthalate and succinate units would

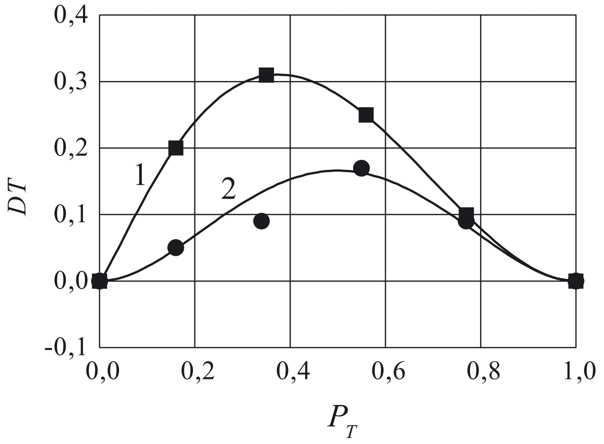


Fig. 4. Degree of transesterification (DT) as a function of terephthalate molar fraction (P_T) depending on amount of catalyst: 1 — 0.5 phr, 2 — 0.1 phr; solid lines are calculated using eq. (9)

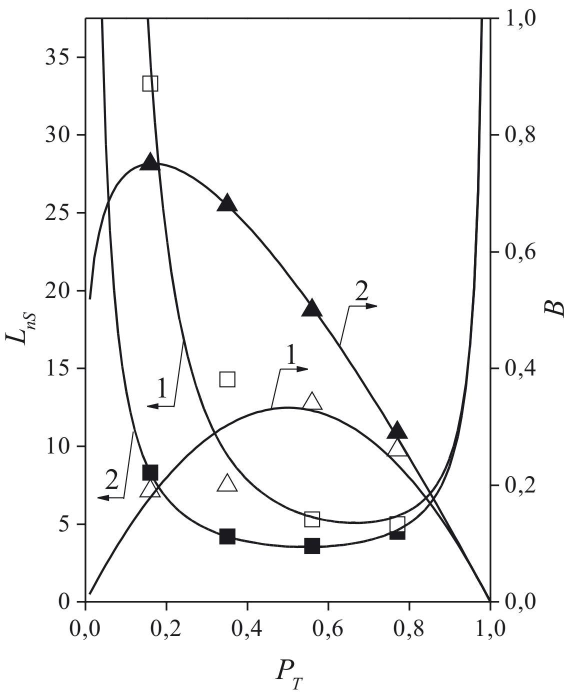


Fig. 5. Block length (L_{ns}) and randomness (B) as functions of terephthalate molar fraction (P_T) depending on amount of catalyst: 1 — 0.1 phr, 2 — 0.5 phr; solid lines are calculated using eq. (9)

lead to $B = 1$ [26]. Figure 5 shows that particularly high B values are observed for blends with high succinate content. The degree of randomness decreases with increasing molar fraction of terephthalate units. This behavior may be attributed to the higher tendency of link cleavage of PTMS under reaction conditions.

Viscosity measurements

From the data discussed so far the question arises whether the transesterification reaction is accompanied by a molecular weight reduction. The value of η_{inh} determined for blend solutions with a constant concentration of 1.055 g/dL may serve as a qualitative measure of molecular weight changes during melt reaction. η_{inh} was measured for physical blends which were not exposed to thermal treatment and for all blends prepared by melt processing. Results are summarized in Figure 6. The η_{inh} slightly decreases with ascending PBT content. The data obtained for the respective blends prepared without catalyst follow the same trend but the inherent viscosities are reduced to approximately 83 % of the values obtained for the blends without catalyst (physical blends). Obviously, this reduction results from the thermal treatment under processing conditions. The action of the catalyst leads to an additional reduction in inherent viscosity. It can be seen in Fig. 6 that viscosity declines more in PTMS rich blends than in PBT rich blends. The inherent viscosity drops down to 47 and 71 % of the values of physical PBT/PTMS 20/80 and 80/20 blends, respectively, when they were processed with 0.5 pph catalyst.

Thermal properties

The thermal properties of the melt processed blends were studied by DSC measurements according to the procedure described in the experimental section. All samples were exposed to the same thermal history before the DSC scans were recorded. Selected results are shown in Table 3. PBT and PTMS are semicrystalline polymers. The glass transition of pure PTMS (T_g^{PTMS}) was detected at -32.5 °C. PTMS exhibits multiple melting peaks. The main peak occurs at 114 °C and is tightly connected with a small cold crystallization peak. Another small endotherm, which is also detectable in most of the blends with PTMS excess (see Fig. 7), appears at about 40 °C. A similar endotherm was also observed by Yoo and Im [29]. In the blends under discussion this endotherm probably covers the glass transition (T_g) of

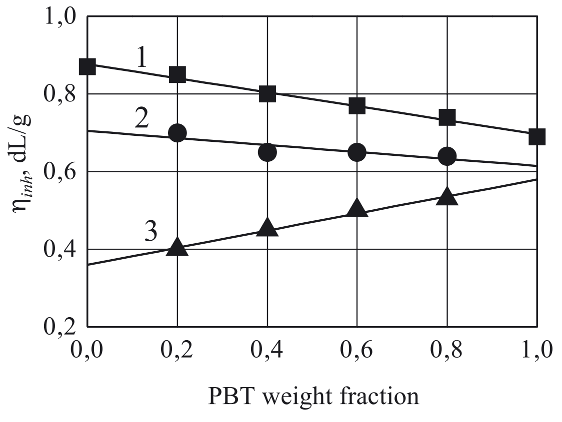


Fig. 6. Inherent viscosity (η_{inh}) of the blends as a function of PBT weight fraction and amount of catalyst: 1 — physical blends, 2 — 0.0 phr, 3 — 0.5 phr; solid lines are regression functions

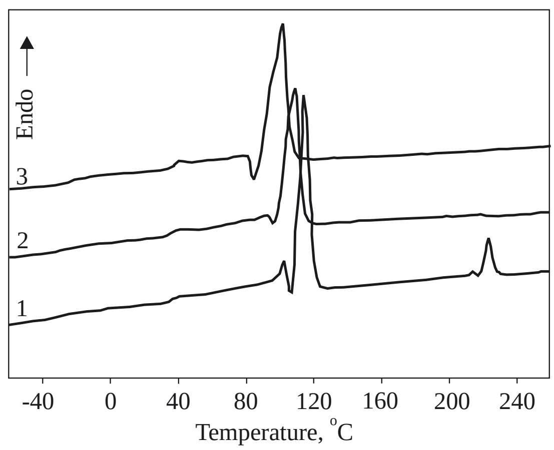


Fig. 7. DSC curves of PBT/PTMS 20/80 blends depending on amount of catalyst: 1 — 0.0 phr, 2 — 0.1 phr, 3 — 0.5 phr

Table 3. Selected thermal properties of PBT/PTMS blends

Blend composition PBT/PTMS	$Zn(CH_3COO)_2$ content, phr	T_g^{PTMS}, °C	T_m^{PTMS}, °C	ΔH_m^{PTMS}, J/g	T_m^{PBT}, °C	ΔH_m^{PBT}, J/g
0/100	0.0	-32.5	113.9	80.7	—	—
20/80	0.0	-31.7	113.8	60.5	222.8	7.8
20/80	0.1	-30.7	108.8	56.6	216.5	0.5
20/80	0.5	-22.7	101.4	51.6	—	—
80/20	0.0	-29.9	112.3	6.8	221.1	41.76
80/20	0.1	-12.7	—	—	215.0	40.9
80/20	0.5	-9.2	—	—	214.1	40.4
100/0	0.0	47**)	—	—	224.5	53.1

*) Ref. [28]. **) T_g^{PBT}.

PBT. The glass transition temperature of plain PBT could not be measured in our DSC experiments, the peak corresponding to melting temperature (T_m) appears at 224.5 °C and is also overlapped by a cold crystallization peak. Fig. 7 displays the DSC scans of PBT/PTMS 20/80 blends. The blend processed without catalyst exhibits the same thermal transitions as the pure components do. No shifts of T_g or T_m can be detected for all blends without catalyst. Addition of catalyst leads to a decreasing melting temperature of PTMS. The melting endotherm of PBT is hard to detect for the blend with 0.1 pph catalyst (Fig. 7, curve 2) and vanishes completely in the blend with 0.5 pph catalyst. The opposite blend PBT/PTMS 80/20 shows complementary behavior. Here the decrease in T_m of PBT from 221 to 214 °C, can be observed whereas the melting peak of PTMS disappears with addition of catalyst.

The blend system PBT/PTMS 60/40 serves as an example of the blends with balanced composition. DSC scans are shown in Fig. 8. Again, the melting endotherms occurring in the blend processed without catalyst are similar to that of the pure components. Transesterification reaction caused by the catalyst leads to dramatic changes in PBT crystallization. The T_m drops down to 179.3 °C, the enthalpy of melting (ΔH_m) decreases from 27.6 J/g to 13.4 J/g for PBT in the blend without catalyst and with 0.5 pph catalyst, respectively. The melting peak of PTMS disappears completely. Complementary effects were observed for PBT/PTMS 40/60 blends.

The values of ΔH_m of the components are summarized in Fig. 9. For the blends prepared without catalyst, it can be seen that the enthalpy of PBT decreases linearly with decreasing PBT content. In contrast, the melting enthalpy of PTMS shows negative deviations from linearity with increasing PBT content. The blends prepared without catalyst have to be considered as heterogeneous blends. During cooling from the melt, PBT crys-

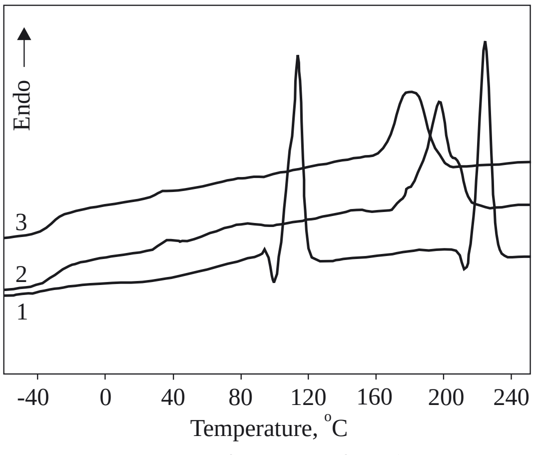


Fig. 8. DSC curves of PBT/PTMS 60/40 blends depending on amount of catalyst: 1 — 0.0 phr, 2 — 0.1 phr, 3 — 0.5 phr

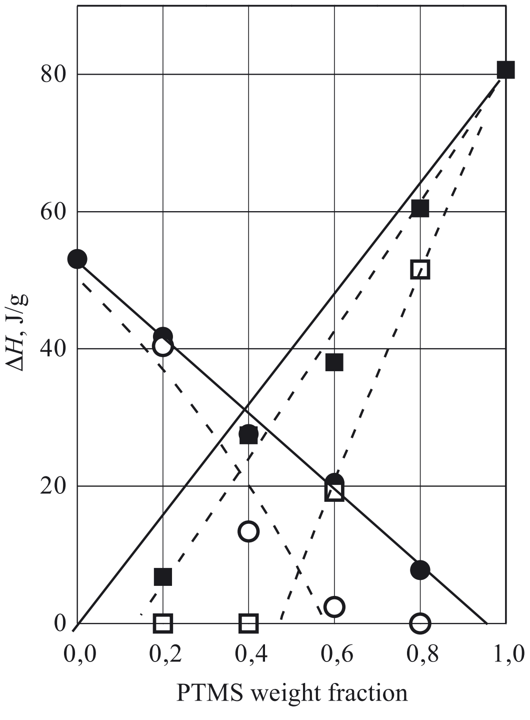


Fig. 9. Melting enthalpy (ΔH_m) as a function of PTMS weight fraction for: • — PBT in the blends without catalyst, o — PBT in the blends with 0.5 phr of catalyst, ■ — PTMS in the blends without catalyst, □ — PTMS in the blends with 0.5 phr of catalyst

tallizes at temperature where PTMS is still in the molten state and PTMS crystallizes in the presence of crystalline PBT. Hence, the degree of crystallinity of PTMS is slightly reduced by crystalline PBT whereas the PBT crystallinity is not influenced by molten PTMS. Similar effects were observed for heterogeneous blends of poly(ethylene terephthalate) (PET) and PTMS crystallized isothermally or non-isothermally from the melt [20].

The enthalpy values obtained after processing of the blends with 0.5 pph catalyst are also indicated in Fig. 9. For PTMS it can be seen that the trend of negative deviations from linearity increases. Under the experimental conditions applied, PTMS crystallization completely vanished due to the transesterification reaction in the blends with PBT excess. The PBT crystallinity does not change significantly in PBT/PTMS 80/20 blends with catalyst, but it drops down with increasing PTMS content and becomes zero in 20/80 blends.

T_g could only be detected for PTMS. No significant change of T_g^{PTMS} can be observed in all blends processed without catalyst. It indicates that PBT and PTMS form heterogeneous two-phase blend systems. Processing of the blends with a catalyst leads to increasing T_g^{PTMS} values as shown in Table 3. It becomes obvious that in the blends with PTMS excess the T_g^{PTMS} increase is more pronounced. The experimentally determined T_g are in all cases lower than those calculated for random copolymers on the bases of additivity.

Morphology of the blends

The crystallization of PBT and PTMS can also be studied by polarizing optical microscopy. PTMS forms large spherulites when crystallized from the melt. One example is shown in Fig. 10. Spherulites of PBT are much smaller and hard to detect and therefore not shown here. The morphology of PBT/PTMS 40/60 blend will serve as an illustration of the blends. Figure 11 shows the situation in the blends without catalyst. A clearly phase separated melt can be seen at a tempera-

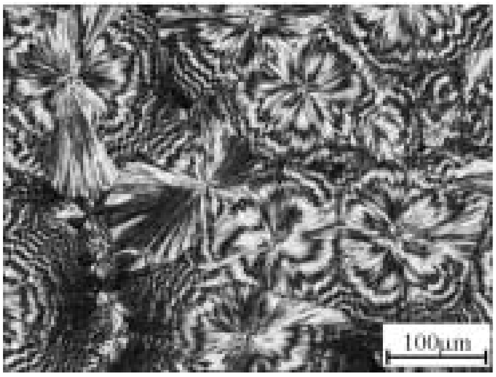


Fig. 10. Polarizing optical image of PTMS crystallized from the melt; image taken at room temperature

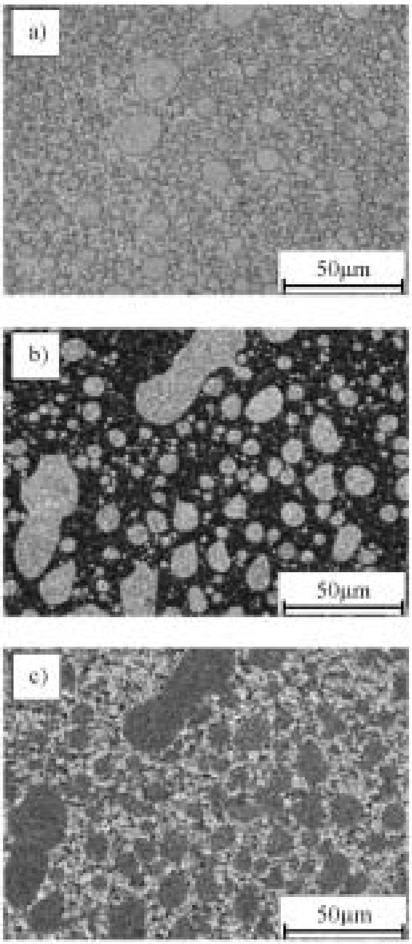


Fig. 11. Polarizing optical images of PBT/PTMS 40/60 without catalyst; images taken at: a) — 260 °C, b) — 140 °C, c) — room temperature

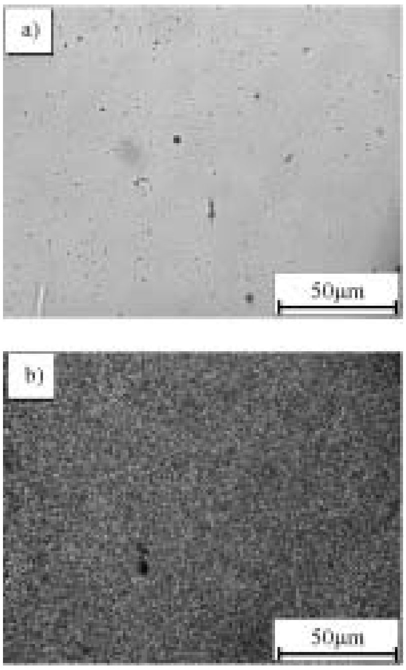


Fig. 12. Polarizing optical images of PBT/PTMS 40/60 without 0.5 phr of zinc acetate at: a) — 200 °C, b) — room temperature after crystallization from the melt

ture of 260 °C (Fig. 11a). Molten PBT droplets are dispersed in a matrix of molten PTMS. Crystallization within the PBT droplets is completed at 200 °C as shown in Fig. 11b. Figure 11c was obtained at room temperature when also the crystallization of PTMS is finished. The two phases are well separated. The PTMS spherulites appear brighter than the PBT spherulites inside the islands. Figure 12 shows the same blend with 0.5 pph catalyst. The phase boundaries in the molten state at 260 °C disappeared completely. Figure 12a displays a clear melt. Figure 12b was obtained at room temperature after crystallization of the melt. Only a very diffuse structure can be seen in polarized light indicating very small crystalline entities, which are homogeneously distributed. No phase boundaries can be detected.

Mechanical properties

Table 4 summarizes selected Charpy impact test data. PTMS exhibits higher impact strength than PBT. It is evident from the results presented that the impact strength declines considerably for the blends without zinc acetate due to immiscibility of both components. Also for PBT/PTMS 80/20 and 20/80 blends with catalyst, the impact values are poor. 20/80 blends were so brittle that no test specimens could be prepared. Nevertheless, the presence of catalyst improves the impact strength of the blends with balanced composition 60/40 and 40/60 to such an extent that specimens did not break during testing.

Table 4. Impact strength of PBT/PTMS blends

Blend composition PBT/PTMS	$Zn(CH_3COO)_2$ content, phr	Notched impact strength, kJ/m^2
0/100	0.0	6.07
20/80	0.0	3.43
20/80	0.1	—
20/80	0.5	—
40/60	0.0	2.90
40/60	0.1	2.34
40/60	0.5	no break
60/40	0.0	4.65
60/40	0.1	no break
60/40	0.5	no break
80/20	0.0	5.76
80/20	0.1	4.54
80/20	0.5	2.52
100/0	0.0	2.67

The tensile properties are illustrated in Fig. 13. The pure polymers and PBT/PTMS 60/40 blends serve as examples. Both PBT and PTMS exhibit a yield point with yield stresses in the range of 45 MPa. The elongation at break for PBT is about 270 % whereas PTMS breaks at around 90 % of elongation. The Young's moduli were determined to be 1456 MPa and 495 MPa for PBT and PTMS, respectively. The situation changes drastically in all the blends without catalyst and in the blends with PBT or PTMS excess as the example of the PBT/PTMS 60/40 blend without catalyst shows (Fig. 13). All those blends break before yielding. The maximum stress drops down to the values between 20 and 40 MPa, the elongation at break is less than 30 %. Only the PBT/PTMS 60/40 blend prepared with 0.1 phr zinc acetate is an exception to this behavior. With increasing zinc acetate content the modulus, yield stress and elongation at break decrease.

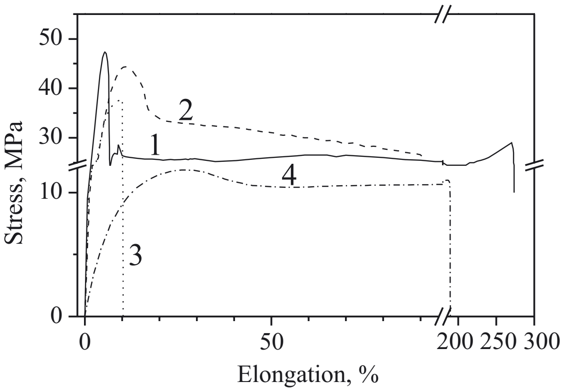


Fig. 13. Stress-strain plots of: 1 — PBT, 2 — PTMS, 3 — PBT/PTMS 60/40 with no catalyst, and 4 — PBT/PTMS 60/40 with 0.1 phr of catalyst

The mechanical properties of the prepared blends are determined by the transesterification reaction and the decline of molecular weight during the transesterification reaction. The molecular weight reduction may lead to the poor mechanical data of blends with 0.5 phr catalyst.

CONCLUSIONS

Melt reactions of PTMS and PBT have been studied to obtain the copolymers with acceptable mechanical properties and sufficient biodegradability. The formation of copolymers containing aliphatic and aromatic units is enhanced by zinc acetate as a catalyst. The process of transesterification is strongly influenced by the amount of catalyst and the initial blend composition. It can be shown by FT-IR and ^{1}H NMR measurements that the copolymer structure changes from a block structure to a more random distribution of units along the chain. The block length decreases slightly with increasing amount of catalyst. Chloroform soluble copolymers were obtained from the blends with PTMS excess. The blends processed without catalyst are heterogeneous and show very poor mechanical properties due to their two-phase morphology. The impact strength of the blends could be markedly improved by the transesterification reaction.

REFERENCES

1. Duda A., Penczek S.: *Polimery* 2003, **48**, 16.
2. Mochizuki M., Mukai K., Yamada K., Ichise N., Murase S., Iwaya Y.: *Macromolecules* 1997, **30**, 7403.
3. Polaczek J., Dziki E., Pielichowski J.: *Polimery* 2003, **48**, 61.
4. Albertson A.-C., Yarma I. K.: *Adv. Polym. Sci.* 2002, **157**, 1.
5. Chiellini E., Cinelli P., D'Antone S., Ilieva V. E.: *Polimery* 2002, **37**, 538.
6. Kim Y. J., Park O. O.: *J. Appl. Polym. Sci.* 1999, **72**, 945.
7. Chang-Sik Ha, Won-Jei Cho.: *Prog. Polym. Sci.* 2002, **27**, 759.
8. Grzebieniak K., Ślusarczyk C., Włochowicz A., Janicki J.: *Polimery* 2002, **37**, 528.
9. Montaudo G., Rizzarelli P.: *Polym. Degrad Stab.* 2000, **70**, 305.
10. Kim Y. J., Park O. O.: *J. Env. Polym. Degrad.* 1999, **7**, 53.
11. Park S. S., Chae S. H., Im S. S.: *J. Polym. Sci: Part A: Polym. Chem.* 1998, **36**, 147.
12. Witt U., Muller R. J., Decker W. D.: *J. Macromol. Sci. — Pure Applied Chemistry* 1995, **A32**, 851.
13. Kint D. P. R., Alla A., Deloret E., Campos J. L., Munoz-Guerra S.: *Polymer* 2003, **44**, 1321.
14. Prowans P., El Fray M., Jursa J.: *Polimery* 2005, **50**, 131.
15. Dae Kyung Song, Young Kiel Sung.: *J. Appl. Polym. Sci.* 1995, **56**, 1381.
16. Nagata M., Goto H., Sakai W., Tsutsumi N.: *Polymer* 2000, **41**, 4373.
17. Ichikawa Y., Kondo H., Igarashi Y., Noguchi K., Okuyama K., Washiyama J.: *Polymer* 2000, **41**, 4719.
18. Ichikawa Y., Suzuki J., Washiyama J., Moteki Y., Noguchi K., Okuyama K.: *Polymer* 1994, **35**, 3338.
19. Ihn K. J., Yoo E. S., Im S. S.: *Macromolecules* 1995, **28**, 2460.
20. Chong K. F., Schmidt H., Kummerlöwe C., Kammer H. W.: *J. Appl. Polym. Sci.* 2004, **92**, 149.
21. Miyata T., Masuko T.: *Polymer* 1998, **39**, 1399.
22. Bormann W. F. H.: *J. Appl. Polym. Sci.* 1978, **22**, 2119.
23. Lyoo W. S., Kim J. H., Yoon W. S., Ji B. C., Choi J. H., Cho J., Lee J., Yang S. B., Yoo Y.: *Polymer* 2000, **41**, 9055.
24. Pisula W.: Master Thesis, University of Wales, UK, 2001.
25. Hopfe L., Pompe G., Eichhorn K. J.: *Polymer* 1997, **38**, 2321.
26. Murano M., Yamadera R.: *J. Polym. Sci.: Part A-1* 1967, **5**, 2259.
27. Murano M., Yamadera R.: *Polymer J.* 1971, **2**, 8.
28. Jackson W. J., Gray T. F., Caldwell J. R.: *J. Appl. Polym. Sci.* 1970, **14**, 685.
29. Yoo E. S., Im S. S.: *J. Polym. Sci. Part B: Polym. Phys.* 1999, **37**, 1357.

Received 28 IV 2005.