

# Mechanical Properties of Polyamide Modified by Block Copolymers: Possible Effect of Tie-Molecules

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Appropriate block ABA copolymers can be suitable agents capable of increasing the number of tie-molecules in the polyamide (PA) blend.

In this work, macromonomers of PA (block A), with backbone chains endcapped with  $\text{—NH}_2$  group on one end, and of polyethyleneterephthalate (PET) (block B), with  $\text{—COOH}$  groups on both ends, have been used. The  $\text{—COOH}$  and  $\text{—NH}_2$  end groups of these macromonomers were reacted *via* condensation reaction joining the A and B blocks to form the desired triblock copolymer PA—PET—PA. Reactions proceeded in a melt in a single screw extruder.

The ABA copolymer was added in different amounts to the PA's matrix. The outside blocks of that copolymer conformed with the polymer matrix and the inner block did not co-crystallize with it. The stress-strain behaviour (yield stress, stress at break, yield strain, elongation at break, and notched impact strength) of these polymer blends was studied as a function of the mole fraction of the inner block. All mechanical characteristics were improved. It is suggested that the improvement can be attributed to the higher amount of tie-molecules in the modified polymeric material.

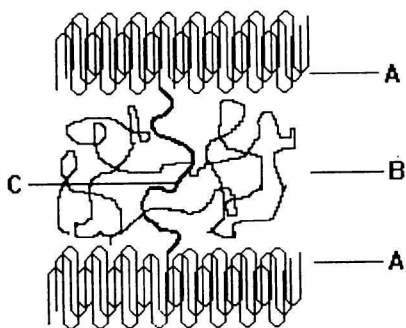
Mechanical properties of semi-crystalline polymers depend strongly on the presence of tie-molecules [1—6]. These are macromolecules or their parts connecting neighbouring lamellae as shown in Scheme 1.

Various ways to increase the number of tie-molecules have been attempted, *e.g.* annealing of the polymer in the solid state [7—10]. More significant results were obtained when mixing modified macromolecules (random copolymer poly(ethylene-co-hexene) or poly(ethylene-co-octene)) with polyethylene. The density of side groups ( $\text{C}_4$  or  $\text{C}_6$ ) affected the thickness of lamellae and the number of tie-molecules [11, 12]. Modification of parts of the macromolecular

systems – combination of reactive chain ends by suitable chemical agent can also be used [13]. Another way to increase the number of tie-molecules seems to be using block ABA copolymers with A blocks capable to be fold into the matrix lamellae. On the contrary, B block should be incompatible with the matrix (Scheme 2). The same (or better) role should be played by copolymers of the H-type as shown in Scheme 3. The first experimentally proved information dealing with this way of the modification of crystalline polymers was published by us [14].

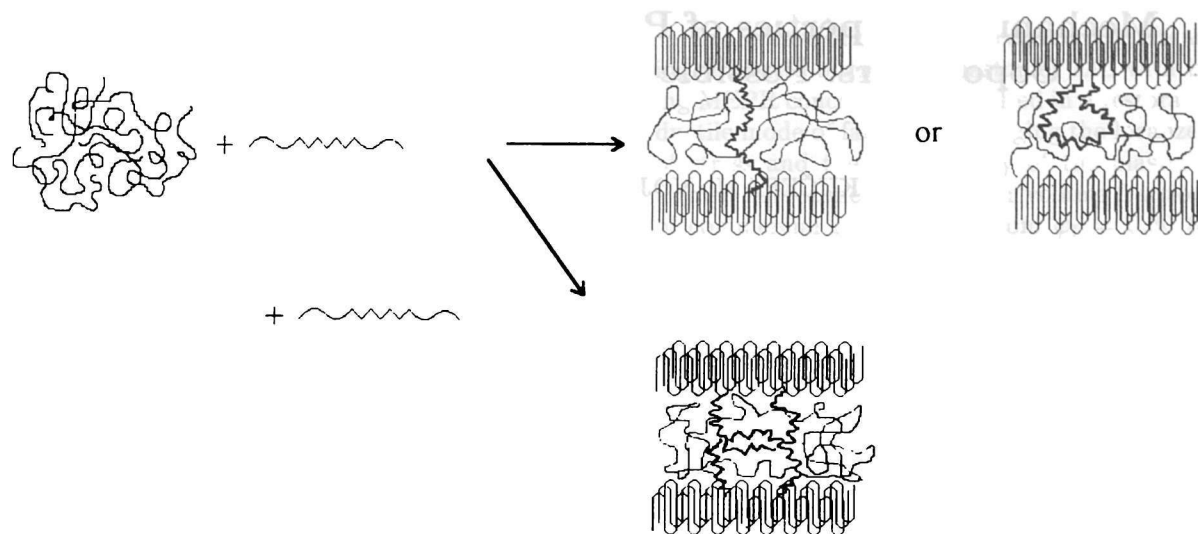
Block copolymers play more and more important role among products of the macromolecular chemistry [13—17]. They are used as the excellent compatibilizers of incompatible polymer blends, polymers, and fillers, as perfect modifiers of interface regions as well as refining additives in general. For their ability to form lamellae, especially copolymers of the ABA type they are of great interest [18—22]. There is still lack of suitable ABA copolymers and a large discrepancy exists between the demand for special types and the synthesis possibilities.

One of the possible ways to obtain ABA copolymers is a reaction of the polymer end groups. The macromonomers endcapped with carboxylic groups  $\text{HOOC—COOH}$  react with the macromonomers of other type containing only one reactive  $\text{—NH}_2$  group. The formation of amido group from  $\text{—NH}_2$  and  $\text{HOOC—}$  is quite easy [23—25]. Synthesis of macromonomers is a topic of numerous papers [26].

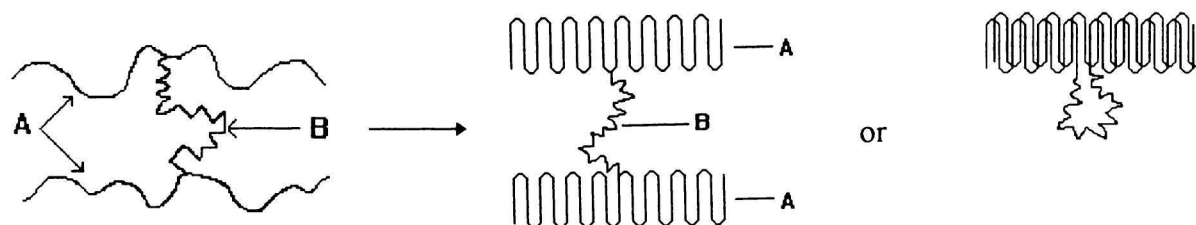


Scheme 1

Tie-molecule connecting neighbouring lamellae. A – lamella from regularly folded chain, B – amorphous phase, C – tie-molecule.



Scheme 2  
Adding ABA copolymer to the A matrix.



Scheme 3  
The H-type copolymer.

Table 1. Characteristics of Macromonomers

Sample code	Type of macromonomer	$[\eta]/(\text{cm}^3 \text{ g}^{-1})$	Extraction part/%	Species content in 1 g of sample $\cdot 10^5/(\text{mol g}^{-1})$			
				molecules	all end groups	active end groups	$(x_r/\%)$
PA 1	$\text{NH}_2\text{—PA—X}$	100	8.2	6.2	12.4	6.2 <sup>a</sup>	50.0 <sup>a</sup>
PA 2	$\text{NH}_2\text{—PA—X}$	147	3.2	4.6	9.2	5.0 <sup>a</sup>	54.0 <sup>a</sup>
PA 3	$\begin{array}{c} \text{NH}_2 \\   \\ \text{NH}_2\text{—X} \end{array}$	125	7.1	5.5	11.0	5.2 <sup>a</sup>	47.3 <sup>a</sup>
PET	$\text{HOOC—PET—COOH}$	30		18.5	37.0	30.2 <sup>b</sup>	81.6 <sup>b</sup>

a)  $\text{—NH}_2$  end groups.

b)  $\text{—COOH}$  end groups.

X  $\text{—COOH}$ .

## EXPERIMENTAL

There are no data describing the influence of voluminous polymeric substituents on the reaction rate of condensation reaction of  $\text{—COOH}$  and  $\text{—NH}_2$  groups. It may be proposed that the probability of group contact diminishes. On the other hand, the high temperature in an extruder will accelerate the condensation reaction. So, prediction of the reaction conditions is almost impossible.

The PA sample (PA 1) containing one amino end group was prepared by polymerization of  $\epsilon$ -caprolactam,  $\epsilon$ -aminocaproic acid, and dodecylamine mixture at 255°C for 7 h under inert atmosphere. The commercial polyamide Spolamid ZP (PA 2), with short side branches, and Chemlon 11 (PA 3), with linear structure, were used also as macromonomers. Analysis of the products is presented in Table 1.

The PET samples containing two  $-\text{COOH}$  end groups were prepared by mixing pre-polymer of  $[\eta] = 5480 \text{ cm}^3 \text{ g}^{-1}$  with terephthalic acid at the content of  $-\text{COOH}$  groups  $5.5 \times 10^{-5} \text{ mol g}^{-1}$  in the melt at  $250^\circ\text{C}$ . Viscosity of the melt decreased rapidly. The parameters of obtained macromonomer are also presented in Table 1. The limiting viscosity numbers were measured using an Ubbelohde viscometer (capillary i.d. = 0.84 mm) with these materials dissolved in the phenol- $\text{CCl}_4$  mixture ( $\varphi_r = 1 : 1$ ) at  $20^\circ\text{C}$ . At least two parallel measurements were executed and the end values were verified using the phenol-*o*-dichlorobenzene mixture.

The  $-\text{NH}_2$  end groups contained in PA were measured by volumetric analysis using 0.04 M- $\text{HClO}_4$  and thymol blue as the indicator. The samples were dissolved in the phenol-methanol ( $\varphi_r = 7 : 3$ ) mixture. The same method with 0.1 M sodium methoxide was used to find  $-\text{COOH}$  end groups contained in PET. The hexanol- $\text{CHCl}_3$  mixture was used as the solvent. In all cases, the measurements proceeded under nitrogen atmosphere.

Yield stress, stress at break, yield strain, and elongation at break of blends were measured using Instron 4466 (Instron Corporation) Tensile Tester at a deformation speed  $50 \text{ mm min}^{-1}$  at  $23^\circ\text{C}$  (ISO 527). Charpy notched impact strength was measured using laboratory pendulum ZWICK 5102 at an impact velocity  $2.9 \text{ m s}^{-1}$  and at  $23^\circ\text{C}$  (ISO 179). Reported values are averaged from five specimens and exhibit standard deviations of 5 % to 10 %.

### Preparation of the Copolymers

The  $-\text{COOH}$  and  $-\text{NH}_2$  end groups of the prepared macromonomers were reacted *via* condensation reaction joining the A and B blocks to form the desired triblock copolymer PA-PET-PA. Reactions proceeded in a melt in the single screw extruder. Kneading and granulation proceeded under following conditions: adjusted temperature  $265^\circ\text{C}$ ; extruder head temperature  $255^\circ\text{C}$ ; real temperature  $253\text{--}257^\circ\text{C}$ ;  $300 \text{ min}^{-1}$ ; flow rate  $0.7\text{--}0.75 \text{ kg h}^{-1}$ ; screw 1 : 4; jet i.d. = 3 mm; plain inlet; pulling equipment; back pressure 0.01–0.02 MPa; torsional moment 7.0–10.5 N m. Injection was carried out at the temperature  $250\text{--}260^\circ\text{C}$ ; injection pressure 25 bar; holding pressure 15 bar; exhaust time 35 s; cooling time 35 s; temperature of mould  $70^\circ\text{C}$ . The limiting viscosity numbers of components and the final blends are summarized in Table 2. Growth of limiting viscosity numbers proves the block copolymer formation.

Products of end groups reaction – block copolymers in pellets – have been added in various amounts into the PA 2 and PA 3 matrix using a screw extruder at  $257^\circ\text{C}$  carried out for 20 min.

Table 2. Copolymers from PA and PET after Kneading

Copolymer No.	Sample	w/%	$[\eta]/(\text{cm}^3 \text{ g}^{-1})$	
			Components	Final
1	PA 1	83.3	80.0	88.0
	PET	16.7	29.0	
2	PA 2	85.8	147.0	91.0
	PET	14.2	29.0	
3	PA 3	86.7	125.0	102.0
	PET	13.3	29.0	

## RESULTS AND DISCUSSION

Basic characteristics of the physical parameters are shown in Figs. 1–8. If the B blocks are not able to participate in lamella forming from the A matrix, they will rest in the amorphous phase and, with certain probability, will form tie-molecules. Figs. 1–5 present dependences of the stress or strain behaviour of polymer blends with the matrix of Spolamid ZP on the mole fraction of the inner PET ( $-\text{CO}-\text{Ph}-\text{COO}(\text{CH}_2)_2\text{O}-$ ) block. Spolamid ZP is a polyamide with short branches along the backbone. The dependences of yield stress and Charpy notched impact strength *vs.* the amount of PET show a maximum. The reliance of the elongation at break on the amount of PET is more complicated. It shows marked minimum at the low content of incompatible chains. Additional measurement (preparation and testing) of samples confirmed the dependence described.

Several pieces of information result from Figs. 1–5:

- Small amount of the ABA copolymer improves physical parameters of polyamide matrix.

- If the A blocks are chemically identical with the matrix, their length has no effect (in the interval studied) on the course of the measured dependences.

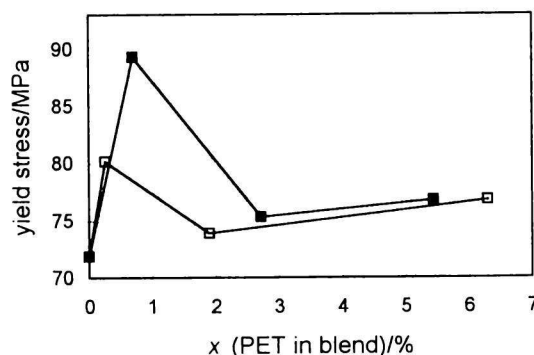


Fig. 1. Yield stress of PA 2 matrix with copolymer *vs.* mole fraction of PET in blend. □ PA 2 matrix and copolymer No. 1. ■ PA 2 matrix and copolymer No. 2.

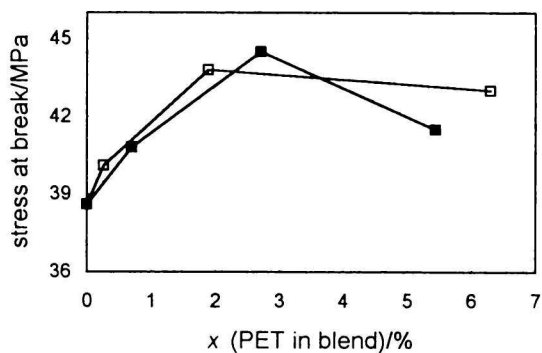


Fig. 2. Stress at break of PA 2 matrix with copolymer vs. mole fraction of PET in blend. □ PA 2 matrix and copolymer No. 1. ■ PA 2 matrix and copolymer No. 2.

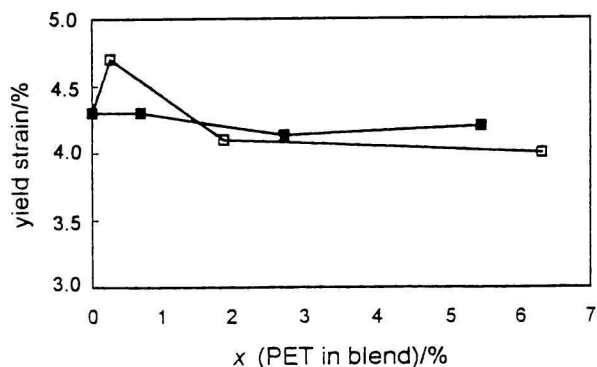


Fig. 3. Yield strain of PA 2 matrix with copolymer vs. mole fraction of PET in blend. □ PA 2 matrix and copolymer No. 1. ■ PA 2 matrix and copolymer No. 2.

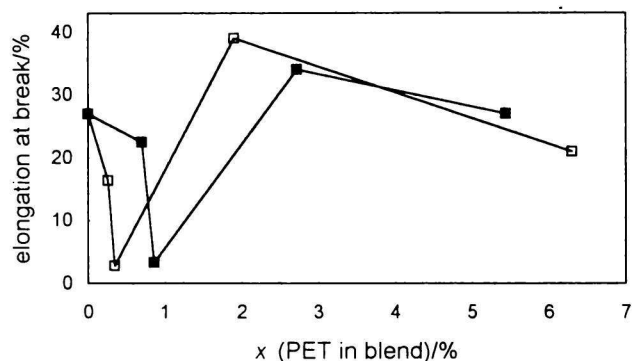


Fig. 4. Elongation at break of PA 2 matrix with copolymer vs. mole fraction of PET in blend. □ PA 2 matrix and copolymer No. 1. ■ PA 2 matrix and copolymer No. 2.

– It will be necessary to investigate the influence of length of the central B block on the physical parameters.

The effect of the ABA copolymer addition into the Chemlon 11 matrix (with markedly less content of side branches) has been tested. In all cases, yield strain, yield stress, and elongation at break grows monoton-

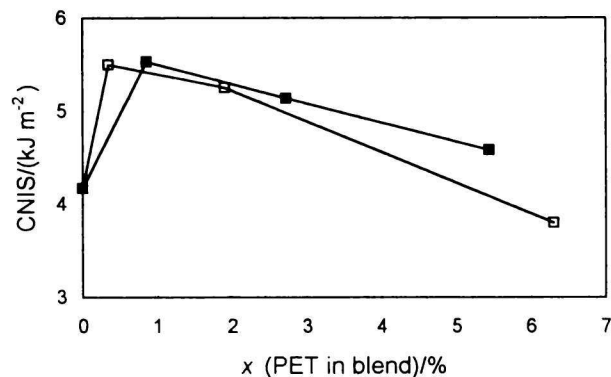


Fig. 5. Charpy notched impact strength of PA 2 matrix with copolymer vs. mole fraction of PET in blend. □ PA 2 matrix and copolymer No. 1. ■ PA 2 matrix and copolymer No. 2.

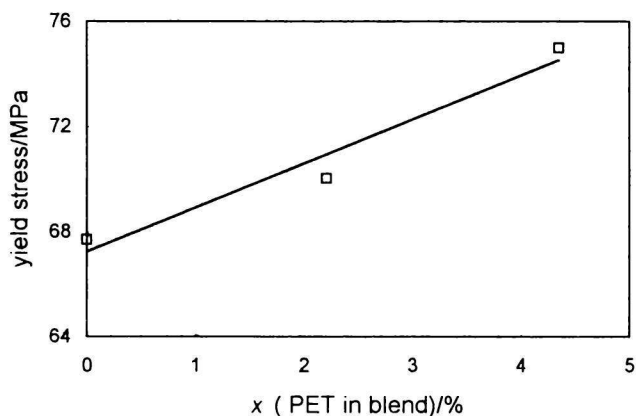


Fig. 6. Yield stress of PA 3 matrix with copolymer vs. mole fraction of PET in blend. □ PA 3 matrix and copolymer No. 3.

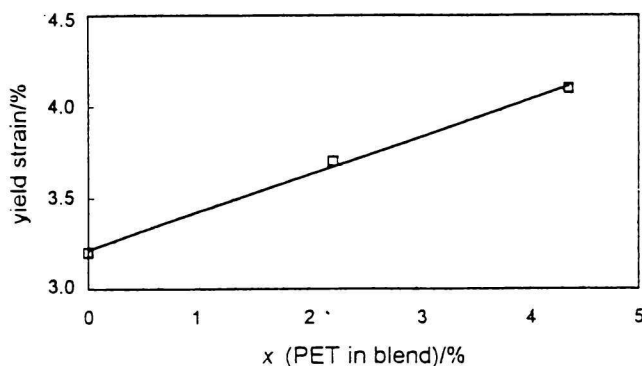


Fig. 7. Yield strain of PA 3 matrix with copolymer vs. mole fraction of PET in blend. □ PA 3 matrix and copolymer No. 3.

ically with the amount of additive (see Figs. 6–8). Notched impact strength is not affected.

The formation of an amide bond between two macromonomers endcapped with  $-\text{NH}_2$  and  $-\text{COOH}$

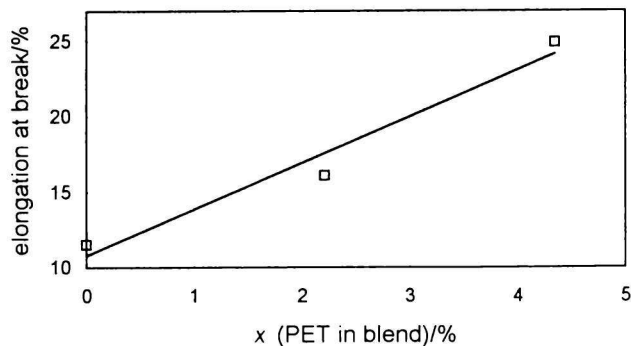


Fig. 8. Elongation at break of PA 3 matrix with copolymer vs. mole fraction of PET in blend. □ PA 3 matrix and copolymer No. 3.

groups in the melt is easy but difficult to verify. The products can be analyzed very hardly. The composition of copolymer is possible to determine only from the kind of endcapped groups and from molecular mass of the resulting copolymer. Our samples eliminated formation of block copolymer including more than three blocks. Diblocks could be formed but the share of remaining macromonomers is still unknown. The little increase of molecular mass of blends after synthesis shows that the content of triblocks capable to enhance the number of tie-molecules can be very low.

The dependence of elongation at break on mole fraction of PET (in the copolymer PA—PET—PA) in PA 2 matrix is interesting. The small amount of PET increases strength but at the same time reduces elongation at break. Sample is broken at higher stress but at lower deformation. This can play an important role in practice.

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