

## Spontaneous polarization of polymer blends

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### Abstract

A hypothesis on the formation of a non-equilibrium in electrical respect structure in blend compositions induced by generation of free charge carriers and their entrapment during extrusion has been put forward. The electret–thermal analysis (ETA) commonly employed to study electrical polarization of dielectrics has been for the first time used to analyze structures of multicomponent polymer blends. Blend composites turned to have characteristic spectra of thermally stimulated currents (TSC). Potentialities of the ETA have been studied on the polyamide–polyethylene blends containing a compatibilizer—bimodal polyethylene functionalized by maleic anhydride. Peaks on TSC spectra have been identified for each component content and their distribution in the blend. Thermomechanical processing of the studied blends even using specific intensive mixing methods (static and dynamic mixing) did not result in the formation of any new chemical compounds. A conclusion has been derived that the formation of electrically non-equilibrium structure is naturally intrinsic for polymer blend composites.

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### 1. Introduction

In the recent decades, structural plastics have been developing chiefly through creation of polymer composites. Polymer blending has proved to be one of the most simple and efficient means of developing high-performance composite systems. Blend composites whose performances surpass those of the initial polymers have served the base for solving a series of technical and economic problems [1,2].

Weak thermodynamic compatibility of polymer components is usually a reason of both low processability and insufficient properties of the blends. Improvement of adhesion between the components is possible by refining their chemical compatibilization, i.e. by introduction of third component, namely a compatibilizer (Cp) into the two-polymer blend [3,4]. Good compatibility is ensured by introduction of Cp based on block and grafted copolymers through improvement of adhesion at the interface and perfect distribution of dispersed polymer components and stabilized structures at the following stages of processing

[5,6]. Commonly, products of monomer grafting to polyolefine macromolecules resulting from reactive extrusion are used as Cp [7,8]. Mechanical and chemical processes at compatibilization are conditioned essentially by the design of reactor, extruder and rigging used [5,9].

In spite of extensive research and a great number of publications in the sphere of reactive extrusion of polymer blends, the nature of processes that ensure compatibility of components and properties of resulting blends have been yet insufficiently studied. To challenge further investigations in the regularities of polymer blend components interaction some new ideas and non-traditional investigation methods are needed.

Components of polymer blends are referred to the class of dielectrics and their thermomechanical treatment in extruder is accompanied by the formation of electrically non-equilibrium structures as a result of breakage of macromolecules, their grafting by polar enzymes, liberation of charge carriers from traps and so on [10]. Electrical polarization of multicomponent dielectrics follows largely the Maxwell–Wagner mechanism. This means that the majority of free charge carriers localizes at the interface between components, provided they differ in their electrical

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properties [11]. In a polymer blend, Cp spreads mainly at the same interfaces due to which spontaneous polarization of blend compositions following Maxwell–Wagner’s mechanism is dependent upon electrophysical properties of Cp. Generated during blend processing polarizing charge might evidently be increased, compensated or leak over the interfaces in the presence of Cp.

A specific characteristic intrinsic for polymer blend compositions is the generation of multitude charge carriers, which are then captured by the traps in structural defects of the composite. Just as the polarity, value and distribution of the charges, from the one hand, so the composite performances (strength, elongation, water absorption, etc.), from the other hand, are the function of the physico-chemical interaction peculiarities of the components and their interfaces properties. It seems logical to anticipate that the pre-history, information on the structure and properties of polymer blend compositions can be of assistance in studying their spontaneous polarization.

The electret–thermal analysis (ETA) is acknowledged in physics of dielectrics as a method reliable for estimating distribution of charged particles in a substance and recording a total electrical moment different from zero. In a number of countries this method used to study the polarizing charge generated in dielectrics at electrical treatment has been regulated by standards [12,13]. The essence of ETA consists in recording the current generated in a specimen and stimulated at heating: disordering dipoles, liberation of charge carriers from traps and their motion.

The idea of the present investigation grounds on the hypothesis that extrusion processing of a polymer blend generates free charge carriers whose entrapment by the surface and bulk traps in the polymer mass induces the formation of electrically non-equilibrium structure of the blend composite. The aim of the work is to estimate potentialities of ETA as a means of studying processes occurring during formation of the polymer blend structure and forecasting its properties.

## 2. Experimental

The following materials have been used for preparation of blends. Polyamide 6 of Tarnamid T-27 grade made at Nitrogen Chemistry plant in Tarnow (Poland) has been dried in vacuum prior to use at 80 °C during 48 h; bimodal polyethylene (PE) of the third generation (Eltex® TUB 120) produced at Solvay (Belgium); bimodal PE functionalized by 0.7 wt% of maleic anhydride (PE-*graft*-MAH) which was prepared according to the methodology presented in Ref. [14] and has been used as Cp.

The specimens as 2 mm thick plates were injection molded from the polymer blends. With this aim a typical single-screw extruder (screw diameter  $D = 16$  mm, length  $L : D = 22 : 1$ ) based on a modified Brabender plastograph (type FOD 234) has been used. Extrusion regimes were the

next:  $T = 220 \pm 5$  °C, rotation frequency of the worm  $n = 50 \text{ min}^{-1}$ , the extruder cylinder was flushed with nitrogen to limit oxidation of macroradicals which resulted from the potential chain scission of the polymers being processed.

The binary PA/PE blends were produced by above equipment with a traditional extruder head. Ternary blends of PA/PE/Cp were melt-mixed by either static or dynamic mixer attached to the extruder (Fig. 1). The static mixer design makes provision for shear rates of the moving melt of about  $50 \text{ s}^{-1}$ . For such shear rate, mixing discs (1) were used, having 12 holes with diameter  $d_1 = 1.2$  mm, and discs (2) having a central hole with diameter  $d_2 = 5$  mm. Discs (1) and (2) have the outer diameter  $d = 39$  mm. Their thicknesses are 4 and 5 mm, respectively. The length of the static mixer in which discs (1) and (2) alternated is 120 mm. The dynamic mixer (Cavity Transfer mixer type) is capable of grafting at the shear rates of  $100 \text{ s}^{-1}$ . The immovable barrel of the mixer was supplied by grooves, and the high speed rotated rotor—by hollows, which provides intensive mixing of blends. The shear rate is calculated as a difference between the linear velocity of the outer surface of the rotor and immovable barrel of the mixer [9].

Stress–strain characteristics of the specimens at tension were determined by a 94-C series tester (Com-Ten Industries Co., USA).

The blends were examined by ETA to obtain their thermally stimulated currents (TSC) spectra based on the method from Ref. [12]. Such an approach is not traditional because the standard ETA method is usually used for

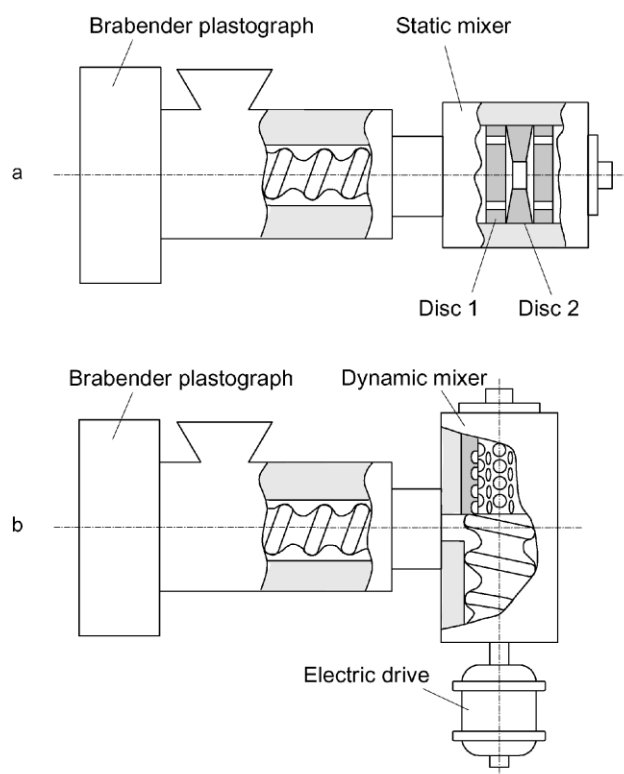


Fig. 1. Diagrams of (a) static and (b) dynamic mixing.

obtaining TSC spectra for dielectric specimens, which are pre-charged or pre-polarized in external electric field, in corona discharge or under some kind of radiation. In our experiments, we have used specimens, which are not exposed to any external electric effects. The spontaneous electric charge is generated in polymer blends during their thermomechanical treatment under conditions of static and dynamic mixing.

A round disc 10 mm in diameter was cut from the molded blend plate and was placed on an earthed aluminum electrode. A Teflon film, annealed at 200 °C to remove technological polarizing charges, was overlaid on the disc. Another aluminum electrode was placed on the Teflon film and the sandwich system was compressed to  $p = 10$  kPa. Current generated in this circuit was recorded during disc heating at about 2.5 °C/min rate. The sandwich system was protected from electrical disturbance by a screen. Weak TSC currents (about a  $10^{-12}$  A value) were registered by an amplifier connected to a PC (the scheme of the device is shown in Fig. 2). Each of TSC spectra shown below has been obtained by averaging the original spectra from not less than five replicate specimens.

The results of TSC analysis were compared to those of DTA (derivatograph Q-1000, weights of  $250 \pm 5$  mg mass, heating rate 5 °C/min). IR spectra of blend specimens were obtained by an UR-20 spectrometer.

### 3. Results and discussion

#### 3.1. Blend components

TSC spectra of blend components under study are shown in Figs. 3 and 4. The spectra for PE and PE-graft-MAH (Cp) display some peaks at 125–126 °C (Fig. 3). This temperature exactly corresponds to the minimum of the endothermal melting peak on DTA curves for PE and Cp. Hence, the peaks on TSC spectra of PE and Cp seem to characterize molecular relaxation processes taking place in crystalline phases at melting. It is interesting that grafting of maleic anhydride to PE macromolecules did not result in a new peak on TSC spectrum. This is the proof that the dipolar fragments of grafted molecules of maleic anhydride neither break-off nor displace within the studied temperature range

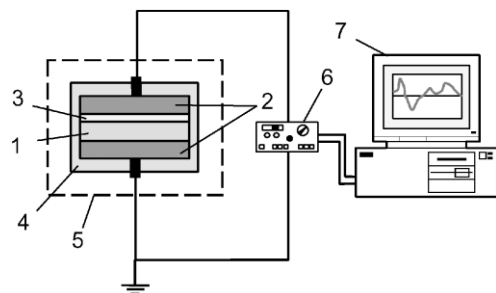


Fig. 2. Schematic drawing of an instrument to register TSC: (1) specimen, (2) electrodes, (3) Teflon laying, (4) screen, (5) thermostat, (6) amplifier, (7) PC.

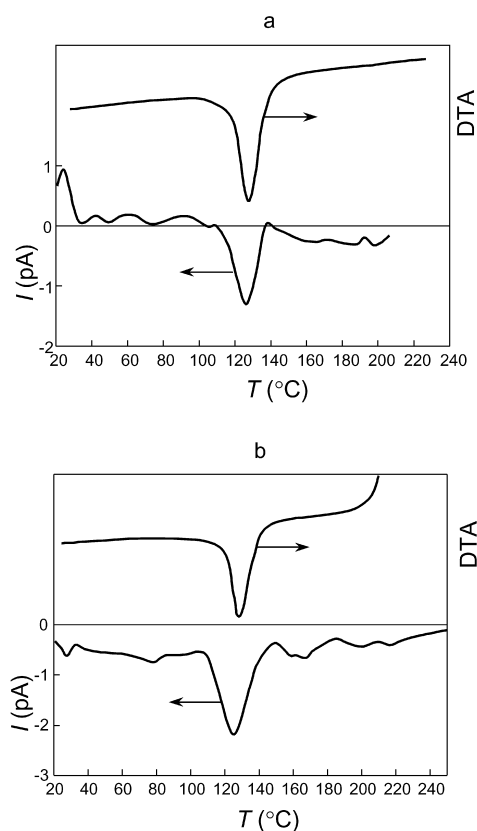


Fig. 3. Temperature dependencies of TSC and DTA curves of (a) bimodal PE, and (b) PE-graft-MAH.

(up to 250 °C). A small peak at 30 °C on PE spectrum corresponds to charge relaxation of the mechano-electret formed during disc cutting from the molded plate.

It has been noticed using DTA method that bimodal PE does not in fact spread at above 200 °C heating of blend components. This is corroborated with the results of estimating the melt flow index (MFI) of the components which was 23.4 g/10 min for PA (at 220 °C, 21 N), and 0.48 g/10 min for PE (at 190 °C, 49 N). So low MFI value hampers much PE processing by injection molding both separately and in blends.

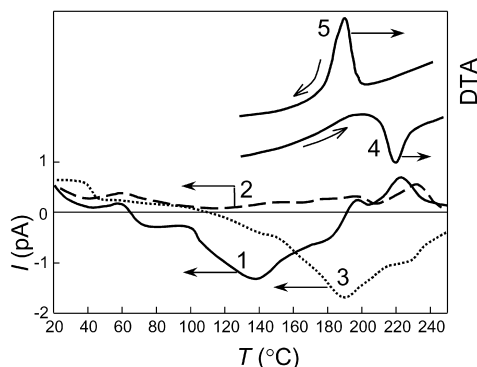


Fig. 4. Temperature dependencies of TSC (1–3) and DTA curves (4: heating–melting, 5: cooling–crystallization) of PA whose specimens: (1) stored for a long time at room temperature; (2) dried out at 140 °C during 2 h; (3) dried and corona charged.

TSC spectrum of PA stored in air (Fig. 4, curve 1) shows peaks at next temperatures:

the peak at 140 °C corresponds to breakage of hydrogen bonds at desorption of bound water adsorbed in the specimen bulk; upon drying the peak disappears (curves 2 and 3);

the peaks at 190–220 °C reflect relaxation of charges formed at thermal decomposition of PA crystalline phase; upon specimen drying (curve 2) all peaks disappear except one that correspond to PA melting point on DTA (curve 4). Upon treatment in corona discharge of the dried out specimen (curve 3) a clear cut peak appears on TSC spectrum exactly corresponding to the temperature of the exothermal maximum of PA crystallization on DTA (curve 5).

Little deviations from the monotonous behavior of TSC curves of PA at temperatures below 100 °C correspond according to Refs. [11,15] to charge relaxation of the mechanoelectret (till 40 °C) and desorption of atmospheric moisture and gases (60–80 °C) from the specimen surface.

### 3.2. Binary PE/PA blend

TSC spectra of binary blends (Fig. 5) have the following characteristic peaks. At 125 °C the peak corresponds to relaxation of the volume charge formed during PE crystallization. The peak at 140 °C is induced, as it has been noted, by desorption of the water absorbed by the specimen during storage. With increasing PA content in the binary blend and reduction of PE amount the peak at 140 °C intensifies whereas that at PE melting point ( $T_m = 125$  °C) diminishes.

TSC spectra of the blends show a small peak with a maximum at 180 °C, which is not typical of the components. This can be attributed to heat-induced rupture of the bonds formed during physico-chemical interaction of components at extrusion. To verify this supposition it is worthwhile comparing them with IR spectra of binary blends and their components (Fig. 6).

Characteristic absorption bands of NH group (3100 and

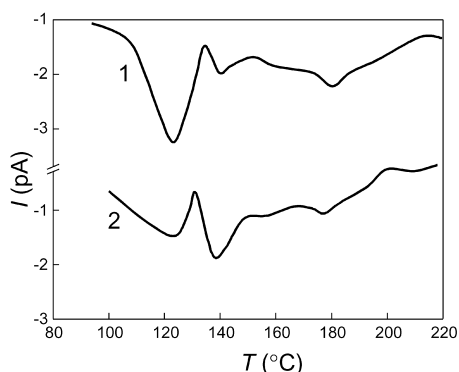


Fig. 5. TSC spectra of binary blends with PE/PA ratio (mass%): (1) 90/10; (2) 50/50.

3360  $\text{cm}^{-1}$  of PA IR spectra) of binary blends shows a shift into the region of lower frequencies (curves 2). At the same time, IR spectrum of the initial PE has an absorption band in 1750  $\text{cm}^{-1}$  region which corresponds to carbonyl oxygen (C=O). It is considered [16] that oxidized PE contains oxygen in the form of carbonyl groups. IR spectra of binary blends show a significant reduction of this band intensity till almost zero and a shift in the region of lower frequencies by 5–10  $\text{cm}^{-1}$  (Table 1). The described phenomena together with a considerable shift (till 30  $\text{cm}^{-1}$ ) of oscillation frequency of NH group in binary blends make grounds for a supposition that physico-chemical interaction of components consists in the formation of intermolecular hydrogen bonds [17] between NH groups in PA and C=O groups in PE. The supposition agrees with the results obtained in Ref. [18] which proved the intermolecular hydrogen bonding between carbonyl groups of novolak/poly( $\epsilon$ -caprolactone) and hydroxyl groups of novolak.

### 3.3. Ternary blend and static mixing

As Cp content in the ternary blend PE/PA/Cp increases, TSC polarity conforming to spontaneous charge relaxation in the specimens changes. Fig. 7 shows that Cp stabilizes the negative and lessens the positive regions of TSC spectra. Spectrum 1 corresponds to relaxation of chiefly hetero-charge, i.e. the polarizing charge whose constituents are the charges of different polarity. With increasing Cp concentration (curves 2 and 3) a tendency is observed to reduce the positive and increase the negative components of the total charge (charge value of each polarity is proportional to the area between the current curve and abscissa line).

As it has been already mentioned, positive TSC within 50–80 °C temperatures is attributed to desorption of water and gas molecules from the atmosphere. These molecules are known to possess low ionizing energy and are easily

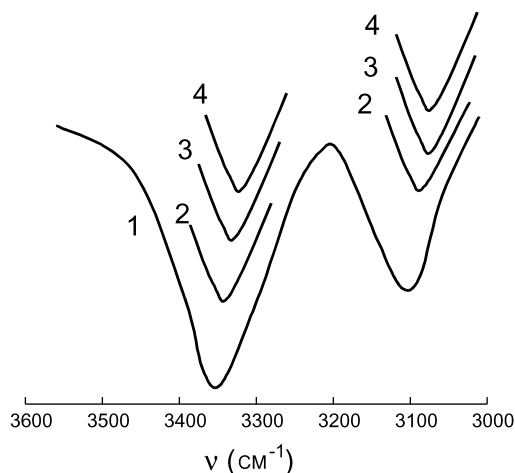


Fig. 6. Location of NH group absorption bands in IR spectra of: (1) PA; (2) binary blend with PE/PA ratio (mass%) 50/50; (3) and (4) ternary blend with PE/PA/Cp ratio (mass%) 45/50/5 after (3) static and (4) dynamic mixing.

Table 1  
IR spectra of blend specimens as a function of their composition and method of processing

Blend components	Group	Absorption band location ( $\text{cm}^{-1}$ )	Shift ( $\text{cm}^{-1}$ ) of absorption band of specimens produced from blends (mass%) using heads		
			50PE/50PA shaping	45PE/50PA/5Cp static	45PE/50PA/5Cp dynamic
PA	NH	3200	20	30	30
		3360	25	35	40
PE	C=O	1750	5–10	10	15
Cp	C=O	1800	–	0	10

transforming into ions [15]. Adsorption of the latter causes dipolar polarization of surface layers of the specimens. Desorption of ions and molecules during ETA changes charge state of the specimen surface and recorded as positive TSC.

It is seen in Fig. 7 that with increasing Cp content in the blend its TSC within  $T = 50\text{--}80\text{ }^{\circ}\text{C}$  lowers which means that desorption reduces. Hence, it can be asserted that adsorption of atmospheric vapors and gases on the specimen surface follow predominantly a physical mechanism. Physical adsorption in the upper surface layer of solids takes up mainly the mechanism of electrostatic interaction between the adsorbent and adsorbate and molecular interactions are imperceptible [19]. Consequently, introduction of Cp into the blend reduces surface charge of the specimens.

### 3.4. Ternary blend and dynamic mixing

The specimens produced by the dynamic mixer from blends containing 10–12% of Cp display the highest charge of spontaneous polarization. Its magnitude is characterized by the area found between the zero line of the current and TSC curve. Fig. 8 proves that under all other conditions being equal, the charge of specimens produced by the dynamic mixer (curves 1 and 2) is considerably higher than that of the specimens formed by the static mixer (curves 3 and 4). It should be underlined that with intensification of mixing the positive portion of the spontaneous techno-

logical charge diminishes and disappears afterwards. Spectra 1 and 2 are in fact consistent with relaxation of the negative homocharge only. The analysis of TSC spectra of all blends studied has confirmed that the least polarizing charge was recorded in the specimens produced by the static mixer from ternary blends containing 70% and more PE.

In our opinion, structure and spontaneous polarizability of polymer blend compositions are interrelated. The polarizing charge value of the specimens is dependent upon the following factors: (i) polarizability of blend components and their thermodynamic compatibility; (ii) interfacial area between structural formations of blend components whose conductivity differs and conditions polarization by the Maxwell–Wagner mechanism [11]. It is believed that high polarizing charge of specimens 1 and 2 (Fig. 8) is ensured by an intensive mixing (dynamic mixer) of the molten polymer blend whose main components (PE and PA) display an elevated mobility when Cp is present. Curves 3 and 4 reflect a less intensive mixing (static mixer), inducing a less charge value.

Evidently, Cp introduction exerts a contradictory effect on the spontaneous technological charge formation. From the one hand, presence of a poor dielectric Cp at the interfaces reduces Maxwell–Wagner's polarization. From the other hand, Cp improves processability of the blend and raises distribution uniformity of components within the blend composition structure. These results in expanded PE/PA interfacial area and, consequently raised spontaneous polarization of the specimens. Besides, the blends containing larger amount of Cp preserve their polarization

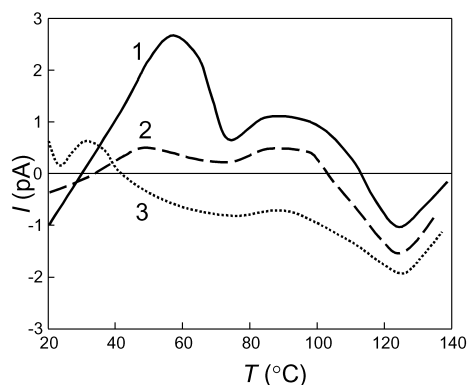


Fig. 7. TSC spectra of specimens produced by a static mixer from ternary blends with PE/PA/Cp ratio (mass%): (1) 85/10/5, (2) 80/10/10, (3) 70/10/20.

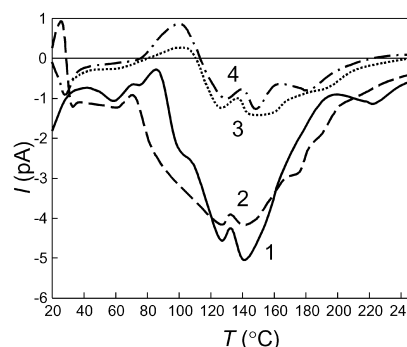


Fig. 8. TSC spectra of specimens produced by a dynamic mixer (1, 2) and static mixer (3, 4) with PE/PA/Cp ratio (mass%): (1 and 3) 10/70/20, (2 and 4) 30/50/20.



at mechanical effect. This is supported by the fact that TSC spectra of all specimens containing 20% of Cp show peaks at 20–30 °C that comply with charge relaxation of the mechanoelectret [15].

Variation in interfacial properties during introduction of Cp into the blends has been recorded by IR spectroscopy. IR spectrum of Cp differs from that of PE by the presence of an absorption band in 1800 cm<sup>-1</sup> region, which is consistent with oscillations of the carbonyl group of the grafted maleic anhydride [17]. The band is much more intensive than that of C=O group of oxidized PE (1750 cm<sup>-1</sup>). The spectra of blend composites show strong shift of characteristic absorption bands of NH group of PA as well as considerable reduction in intensity and shift into the region of low frequency bands corresponding to carbonyl groups of PE and Cp (Table 1). This can be a proof that these groups participate in the formation of intermolecular hydrogen bonds with NH groups of PA.

Thus, the magnitude of the spontaneous polarizing charge of blend specimens and their TSC shape carry certain information on distribution of components in the composite structure and, consequently, on its mechanical properties. This is supported by the comparison of TSC spectra and the values of mechanical strength of the specimens.

The analysis of stress–strain diagrams of the specimens studied (Fig. 9) have shown that PE, PA (curves 1 and 2) and their binary blends (curve 3) fail at tension like typical partially crystallizing polymers. There are some sections on the diagrams reflecting strain growth in proportion to stress, those of violated proportionality and the sections of flow and growth of viscoelastic strain upon reaching stress  $\sigma_e$  (limit of forced elasticity) terminating in rupture of the specimen under test. Diagrams for Cp and ternary blends (curves 4 and 5) display a specific view peculiar to glassy polymers, with a large difference between  $\sigma_e$  and stress according to flow state. Flow sections are rather long (>600%).

The specimens whose TSC spectra are shown in Fig. 8

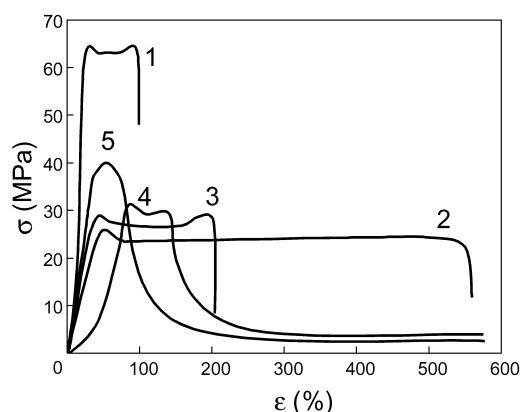


Fig. 9. Stress–strain diagrams of specimens: (1) PA; (2) PE; (3) binary blend with PE/PA ratio (mass%) 30/70; ternary blend with PE/PA/Cp ratio (mass%) 10/70/20 after (4) static and (5) dynamic mixing.

have the following  $\sigma_e$  values: 1 and 2—40 and 37 MPa, 3 and 4—31 and 27 MPa, correspondingly. Hence, a substantial spontaneous technological charge of a blend composite can be considered as a sign of improved strength.

#### 4. Conclusions

- A. Polymer blend composites possess electrically non-equilibrium structure which, when heated, generate currents recorded by the ETA.
- B. Introduction of a Cp into blends initiate processes exerting a competing effect on the spontaneous polarizing charge value of the blends. From the one side, presence of Cps, which are known to be poor dielectrics at the interfaces, alleviates Maxwell–Wagner’s polarization in blend specimens. From the other side, Cps raises processability of blends and distribution uniformity of components inside a composite. This widens interfacial area and, hence intensifies spontaneous polarization of the specimens.
- C. Cps initiate physico-chemical interaction between blend components through formation of intermolecular hydrogen bonds leading to some lessening of the spontaneous polarizing charge in blend composites.
- D. Intensified mixing of polymer components at processing raises spontaneous polarization of blend composites arising from Maxwell–Wagner’s mechanism.
- E. ETA turned to be a sensitive method of studying structure and pre-history of polymer blend composites. In combination with other traditional procedures for studying polymers ETA helps to estimate distribution of components in a blend and degree of their physico-chemical interaction which, in their turn, ensure mechanical properties of composite plastics.

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