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TITLE: Structure and Elastic Properties of Immiscible LDPE-PP Blends:
Dependence on Composition

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This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings Volume 740
Held in Boston, Massachusetts on December 2-6, 2002. Nanomaterials for
Structural Applications

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Structure and elastic properties of immiscible LDPE-PP blends: dependence on composition

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ABSTRACT

Local elastic properties and microstructural features of low-density polyethylene-polypropylene (LDPE-PP) blends have been studied by microacoustical technique, differential scanning calorimetry and infrared spectroscopy. Focused ultrasonic beam of acoustic microscope has been employed to measure elastic wave velocities, bulk and shear elastic moduli and Poisson ratio. The experiments show that the mechanical properties of immiscible LDPE-PP blends are non-additively changeable in relation to ones of primary homopolymers. Maximum of the moduli values is achieved with small addition of LDPE to PP. Additional drawing of bipolymer shows essential increasing of orientation ability for PP chains in 5/95 – 10/90 % LDPE-PP compositions. DSC curves show no significant deviations in melting temperature and crystallinity degree for different compositions of PP and LDPE phases. Internal microstructure has been imaged for the blends by acoustic microscopy technique. It allows revealing dispersivity of components over the blend body.

INTRODUCTION

Mixing of the polymers leads to production of materials with positive properties omitting more expensive stages of the new polymer synthesis. Polyolefins are the main components of plastic wastes and scrapes [1] and their regeneration as a blend has a practical importance. One of the most extensively studied polyolefins are polyethylene and isotactic polypropylene. Many papers are devoted to investigations of the polyethylene-polypropylene blends [2-4]. Mechanical property of the blends and their relation to structural organization is one of the most attractive topic of consideration. Polymer mixing can lead to improvement of the properties [5]. Variation in properties depends on blend composition, morphology and interaction between phases as well as synthesis conditions [6,7].

A series of structure sensitive methods was used in this study – DSC, IR-spectroscopy and acoustic microscopy techniques (AM). In particular, modern ultrasound methods appear a valuable tool for the local elastic property characterization (compressive as well as shear elastic moduli) and monitoring of internal microorganization [8].

EXPERIMENTAL

Material

Isotactic polypropylene (PP) ($T_m = 159.6^\circ\text{C}$, $\chi = 47\%$, $\rho = 0.9076\text{g/cm}^3$, $M_w = 400\,000$, $M_n = 150\,000$, $M_w/M_n = 2.7$) and polyethylene (PE) ($T_m = 106.1^\circ\text{C}$, $\chi = 22\%$, $\rho = 0.9271\text{g/cm}^3$, $M_w = 80\,000$, $M_n = 30\,000$, $M_w/M_n = 3$) were the objects under investigation. The extrusion method of the blend preparation is described in [9]. Isotropic films have been fabricated by pressing with

cellophane substrate at temperature of 190 °C with following quenching in water (0 °C). Thickness of PE-PP films was ~ 200 µm.

Acoustic microscopy

Methods of quantitative acoustic microscopy have been applied to measure local elastic properties and their distribution in polymer blends [8,10]. Short probing pulses of high-frequency focused ultrasound (with pulse duration 30-70 ns and operation frequency 50 MHz) are excited in a coupling fluid and interact with a specimen placed in the focal region (focal spot was 50-90 µm diameter). The probing beam partly reflects from the specimen face, partly penetrates into the specimen as two convergent beams of longitudinal (L) and transverse (T) waves. Both of the beams undergo reflection and mode conversion (LT) at the back surface of the specimen. The output signal of the acoustic microscope is a series of echo pulses. The pulses are separated in time by intervals τ_L , τ_{LT} . Values of sound velocities in a specimen under investigation (d – specimen thickness) are expressed through these intervals:

$$c_L = \frac{2 \cdot d}{\tau_L}; \quad c_T = \frac{d}{\tau_{LT} - \frac{1}{2} \cdot \tau_L}. \quad (1)$$

Data on acoustic wave velocities can be applied to elastic moduli calculation [11].

The technique demands solid identification of echo-signals. If a specimen possesses bulk microstructure (for instance, contains extended defects, pores, phase interfaces and so on) the output signal of the acoustic microscope involves additional sets of echo pulses stemming from reflection at these details. The additional signals can be used to form acoustic imaging (C-scans) for studying topology of the inclusions inside of the specimen body. Another type of acoustic images is B-scans that are formed as traces of echo signals along scanning direction.

Differential scanning calorimetry (DSC)

Degree of crystallization and melting temperature has been studied by DSC technique [12,13]. DSC thermograms were obtained on a DSM-2M differential scanning calorimeter by heating at 8 °C/min. Average value of the melting temperature was measured by maximum of the melting peak in DSC thermograms.

Polarised infrared spectroscopy (IR)

IR-spectra of polymer blend and undiluted components were carried out on "Specord IR-71" spectrophotometer. Degree of orientation was characterized by band dichroism at 840 cm⁻¹ and 710 cm⁻¹ for PP and PE, correspondingly [14,15].

RESULTS AND DISCUSSION

Acoustic microscopy

Basing on time-delays (τ_L , τ_{LT}) measuring and geometry (d) data the longitudinal C_L and transverse C_T wave velocity have been calculated (equation 1). Poisson's ratio μ , bulk K and shear G elastic moduli have been derived from the data on sonic velocity and density for different compositions of the LDPE-PP blend. Density ρ was measured by the Archimedian principle (accuracy was 0,005 g/cm³). Results of the measuring and calculations are presented in Table I. The data is given after averaging over three samples for each composition. Elastic moduli show higher

values than those found in tensile tests [2]. This difference can be result from variation in polymer morphology, methods of preparation and, probably, from probably influence of relaxation processes [16]. The employed frequency of 50 MHz is much higher than characteristic frequencies for many relaxation processes in PP and PE.

Our experiments give values of the elastic moduli of LDPE-PP blend are essentially higher than moduli of individual homopolymers in the wide range of compositions. It means the rule of additivity is invalid for the LDPE-PP mixture. Starting from pure PE increasing the PP content in blend composition results in growth of elastic moduli. The growth is accompanied by oscillations that form series of intermediate maxima and minima. These features are inherent in all types of the moduli - bulk K and shear G moduli and Young modulus E . In our experiments 10, 35, 70 and 95 wt% PP containing blends are characterized by occurrence of local maximums of the velocity value and moduli. Absolute maximum of elastic property is achieved for the blend with 95% PP. Figure 1 shows behavior of elastic wave velocity in depend on the blend composition. We plot values of sonic velocity for three identical specimens for each composition. It can be seen that values of local maxima and minima are varied a little from one sample to another but the general character of the dependence remains the same. Earlier papers reported about the same behavior of elastic moduli for LDPE-PP blends with growth the PP content [17-21]. Position of the absolute maximum can vary and correspond to a little different bipolymer composition. The difference between experimental data shows that the mechanical properties of blends are probably affected by the mixing conditions.

Variation of elastic characteristics observed in our experiments can be evidence that the different PE-PP compositions possess a diverse structural organization. The correlation between mechanical properties and PE-PP blend morphology has been studied by *Lovinger A. et.al.* [2], which showed that the PE could be considered as an agent of stiffness increasing for PP matrix. The recent article [22] report about structural transformation of polyethylene phases in PE-PP blends; some authors [23] reported that polypropylene and polyethylene could be miscible at some crystallization temperatures.

Values of elastic characteristics for the blend with small PE addition surpass the elastic moduli of pure PP and PE.

Table I. Longitudinal C_L and transverse C_T velocities for different composition of PE-PP blend Accuracy of measurement 2,5% and 1% for longitudinal and transverse wave velocities respectively; K and G are bulk and shear elastic moduli; E is Young modulus; μ is Poisson ratio.

PP-PE %	ρ , g/cm ³	C_L , km/s	C_T , km/s	K , GPa	G , GPa	E , GPa	μ
0/100	0.93	2.09	0.83	3.15	0.62	1.75	0.41
10/90	0.93	2.24	0.99	3.37	0.90	2.48	0.38
20/80	0.93	2.09	0.91	2.96	0.76	2.11	0.38
35/65	0.92	2.51	1.10	4.28	1.10	3.04	0.38
50/50	0.92	2.26	1.00	3.43	0.92	2.53	0.38
70/30	0.92	2.53	1.11	4.38	1.13	3.11	0.38
80/20	0.91	2.38	1.07	3.78	1.06	2.91	0.37
90/10	0.91	2.52	1.14	4.29	1.20	3.30	0.37
95/5	0.91	2.63	1.17	4.68	1.27	3.50	0.38
100/0	0.91	2.20	0.94	3.11	0.83	2.28	0.38

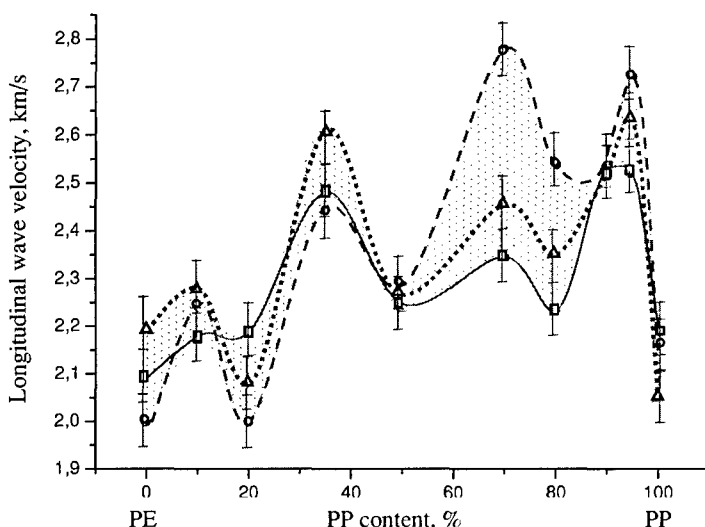


Figure 1. Effect of the PE-PP blend composition on elastic wave velocity. Longitudinal wave velocity has been measured for the three sets of the blend compositions. Different lines show values for different samples.

This peculiarity can result from increasing elastic moduli of blend components caused by mutual influence of one components to structure of the other. It is possible strong affect of interfacial layers between phase domains on acoustic property of the blend.

LDPE-PP mixtures tend to separate into individual phase clusters. The acoustic images (B- and C-scans) of the 50-50 wt% PE-PP composition are presented in figures 2a,b. The B-scan gives a cross-section of a blend sample; the C-scan visualizes structure of a internal layer parallel to the specimen face.

The images are formed by echoes are recorded within a fixed time interval. The interval can include echo signals from the whole specimen (1D scanning in this case gives the B-scan shown in figure 2a) and only a part of it (2D scanning over the specimen in this case gives the C-scan shown in figure 2b). Contrast of acoustic images is caused by variations in signal amplitudes and, accordingly, in reflectivity of phase interfaces.

Acoustic images 2a and b include reflections from interphases, which are seen as bright lines or domains. Sizes and distribution of these details characterize the phase dispersion of the blend. The same internal structure with numerous interfaces is characteristic for quite a wide range of concentrations: 30-70 wt% PE-PP ... 35-65 wt% PE-PP. Number of details in acoustic images diminishes for low concentration of PE or PP.

It is difficult to associate directly the remarkable PE-PP blend morphology with variations in elastic moduli. Stiffening the blend for high PP content as well as the moduli oscillations could originate as from formation of interphase compatibilized transition layers so from bulk effects of mutual influence of polymer networks.

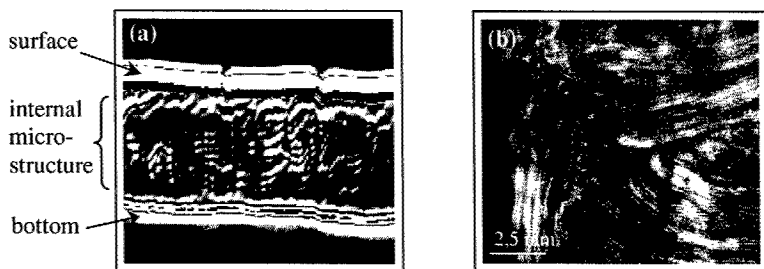


Figure 2. Acoustic images of PE-PP blend with 50-50 wt.% composition: (a) B-scan with numerous internal microreflections; (b) C-scan with phase or elastic properties distribution of the blend.

Differential scanning calorimetry (DSC)

The melting temperature for the undiluted PP and PE is different ($T_{m\text{PP}} = 159.6^\circ\text{C}$ and $T_{m\text{PE}} = 106.1^\circ\text{C}$); as a result their structures are formed separately. The DSC curves have been used to detect melting temperature and crystallinity dependence on the blend composition. Results of investigation are presented in Table II. DSC curves show no significant deviations in melting temperature and crystallinity degree for different compositions of PP and LDPE phases.

PP-PE wt %	Crystallinity degree, %		Melting temp., $^\circ\text{C}$	
	PP	PE	PP	PE
0/100	—	22	—	106.1
10/90	42	21	159.6	106.6
20/80	43	22	159.1	106.6
35/65	41	18	159.1	107.1
50/50	45	17.5	160.6	106.6
70/30	42	16	159.6	105.6
90/10	41	18	160.1	107.6
95/5	44	15	160.1	105.6
100/0	47	—	159.6	—

Table II. Melting temperature and crystallinity degree dependence on the PE-PP blend composition,

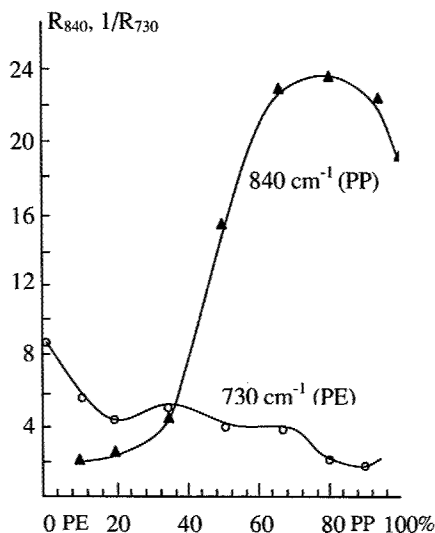


Figure 3. Effect of the PE-PP blend composition on orientation degree R .

Infrared spectroscopy (IR)

The study of the oriented PE-PP system by IR-spectroscopy shows that increase of orientation degree for the PP starts nearby 35 wt% and achieves the maximum for the 80-20 wt% PP-PE blend (figure 3). At small percents PP does not form continuous structure and is involved in PE matrix as discrete structural elements. In this case, the applied stress induces orientation processes in PE matrix while PP grains are weakly deformed only.

CONCLUSIONS

Study of elastic properties for the PE-PP blend carried out by microacoustical technique shows non-monotonical dependence on blend composition. As increasing the PP content elastic moduli of the blend are growing accompanied by formation of intermediate maxima and minima. The absolute maximum is achieved for high PP content but not for pure PP. Apparently, the PE-PP mixture is not absolutely immiscible as accepted. The components influence mutually on their state. Acoustic images of the blend microstructure show laminate dispersion of the polymer phases. Poor adhesion at interphases as well as formation of a new stiffer phases can cause presence of numerous reflectors in the specimen body of the PE-PP system. Results of our elastic moduli measurements force us to support the second explanation.

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