

Thermal Analysis, Mechanical and Rheological Behaviour of Melt Manufactured Polyethylene/Liquid Crystal Polymer Blends

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Modification of properties of conventional thermoplastics with thermotropic liquid crystal polymers, from one hand, allows decrease their viscosities, substantially facilitating processing conditions, and, from another hand, allows increase their exploitation properties. Orientation of the labile structure of liquid crystal polymer in extrusion or injection moulding causes specific reinforcement (so-called self-reinforcement) to occur in the blends containing liquid crystal polymer. Up to now the effect of self-reinforcement is mostly investigated in the blends, containing considerable amount of liquid crystal polymer.

In this research the effect of minor amounts of liquid crystalline co-polyester modifier on the properties of polyethylene is investigated. Various compositions of laboratory synthesized hydroxybenzoic acid /polyethylene terephthalate copolymer containing polyethylene composites have been manufactured by thermoplastic blending.

It has been observed that 1) modulus of elasticity, yield strength and ultimate strength increase with raising the content of liquid crystalline modifier; 2) void content in the investigated polyethylene/liquid crystal copolymer composites is not greater than 1 %; 3) addition of liquid crystalline co-polyester modifier improves arrangement of PE crystalline phase.

Keywords: polyethylene, thermotropic liquid crystalline polymer, synthesis, structure, mechanical, rheological properties.

INTRODUCTION

Polymer blends have many advantages over chemically homogenous materials due to possible interaction between the components allowing produce practically new materials with interesting set of properties, distinct from those of base polymers. Besides it, polymer blends can be formulated, optimized and commercialized at a much faster rate than newly synthesized polymers (considering that there are no serious compatibility problems between the components), thus satisfying the growing demand for new materials. Consequently manufacturing rates of polymer blends increases year by year, outpacing the growth rate of existing polymers by at least 2 % to 5 % [1]. The current worldwide market volume for polymer blends is estimated to be more than 700 000 metric ton/y, with an average growth rate of 6 % to 7 % [1].

Interest in the problem of modification of exploitation properties of conventional thermoplastics by thermotropic liquid-crystalline co-polyesters (LCC) is generally explained by two aspects: decreased melt viscosity of the composites, which considerably promotes their processing into consumer products [2–3], and substantial increase of their mechanical properties due to the formation of reinforcing liquid-crystalline fibrils [4–6]. Upon extrusion or injection moulding of LCC-containing thermoplastic compositions, characteristic reinforcement of the material occurs due to stretching of the liquid crystalline inclusions

into anisodiametric ellipsoidal formations. Although, the effect of self-reinforcement usually is characteristic for extruded and stretched composites containing considerable amounts of LCC (up to 30 wt% and more) [7], in our earlier work [8] we have observed this phenomena also for polyethylene (PE) composite at small concentrations of high-melting liquid crystalline polymer. In our earlier work [8] it has been also shown that experimentally observed growth of elastic characteristics along with increasing LCC weight ratio (especially at higher weight content) is somewhat slower than that, calculated theoretically. One of the reasons for such behaviour is ineffective orientation of LCC fibrils in the polymer matrix. Another possible reason could be subjection of polymer matrix to high processing temperatures of LCCs, outreaching melting temperature of polyethylene by more than 80 °C.

Considering possible thermo-oxidative destruction of PE at processing temperatures of conventional high-melting liquid crystalline polymers (such as Vectra 950A and Vectra 950B), in this research modification possibility of PE with medium melting temperature (ca 200 °C) LCC is investigated.

EXPERIMENTAL

Polyethylene (PE, EgeyopteneMD 3804, Egyptian European Company) with melt index of 4 g/10 min and melting peak temperature of 128 °C has been used as matrix material. Medium melting temperature liquid crystalline copolymer (LCC) modifier has been synthesized in laboratory from following chemicals: 4-hydroxybenzoic acid (HBA, Sigma-Aldrich, purity ≥99 %), acetyl chloride

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(Sigma-Aldrich, purity 98 %), pyridine (Lach-Ner, Czech Republic, purity – 99.5 %), methanol (Acros), concentrated HCl, polyethylene terephthalate (PET, Polyclear T-86, Hoechst T86). Before the synthesis of LCC pyridine has been dried for 24 hours on KOH pellets (Acros – purity 99.99 %) and purified by vacuum distillation.

Synthesis of TLCP HBA 60 % / PET 40 % has been carried out in two steps: 1) acetylation of HBA and 2) esterification of the obtained 4-acetoxybenzoic acid (ABA).

Preparation of 4-acetoxybenzoic acid (ABA). 4-hydroxybenzoic acid (0.670 mol) has been dissolved in pyridine (1.285 mol) in 500 ml three-neck glass flask. Acyl chloride has been added very slowly during 1 hour while stirring in ice bath at the temperature below 0 °C. After adding all of the acyl chloride the mixture has been stirred for about 30 min in ice bath and for 1 h in room temperature. The mixture has been poured in ice-cold water and pH has been reduced down to 1–2 by adding concentrated hydrochloric acid. The white precipitate has been washed with ice-cold deionised water and dried on Na₂SO₄ in a desiccator. Finally ABA has been re-crystallised from water/methanol mixture (1:1). The product has been obtained in the form of white needle like crystals with 97 % purity (96 % yield), m.p. 181 °C–183 °C. The structure has been confirmed with ¹H NMR (DMSO-d₆): δ 10.5 ppm, (br. singlet H of –COOH), 8.1 ppm (doublet 2H aromatic, ortho to –OAc), 7.3 ppm (doublet 2H aromatic, meta to –OAc), 2.3 ppm (H broad singlet of –CH₃).

Synthesis of ABA 60 % / PET 40 % co-polyester (LCC). Synthesis of ABA 60 % / PET 40 % co-polyester has been made by modification the synthesis of W. J. Jackson and H. F. Kuhfuss [9]. 4-Acetoxybenzoic acid (0.058 mol) and polyethylene terephthalate (0.056 mol) has been mixed in a 100-mL three neck glass flask equipped with a gas inlet (for analytically pure nitrogen), thermometer and distillation column with nitrogen outlet, connected to it. The distillation system has been connected with small tube for by-products (water, acetic acid), and the end of it has been connected through Tischenko tube (with KOH) to vacuum source (oil vacuum pump).

The three neck glass flask has been set into the specially made bath (modification of Wood's bath) with a magnetic stirrer. The system has been made to let the stirring process by magnetic stirrer in the flask and also to keep the desired temperature during the polycondensation process.

The reaction flask has been purged with nitrogen (gas flow – 400 ml/min) for about 10 minutes to remove air and then it has been heated for 10 minutes over the metal bath at 110 °C to dry the reactants. The flask has been placed into the bath. The metal bath has been heated up to 275 °C while purging with small flow of nitrogen (50 ml/min).

While the contents have been stirred in a nitrogen atmosphere, acetic acid slowly distilled out. After low melt viscosity product has been obtained (60 minutes), a vacuum of about 133 Pa has been applied and stirring has been continued for about 4 hours at 275 °C. Consequently white high melt viscosity product has been obtained (yield 95 %), m. p. 202 °C. FT-IR (Br): 3453 (OH), 2965 (CH₂),

1721 (C=O), 1604, 1504 and 1406 (aromatic), 1336–1010 (C–O), 850–670 (aromatic) cm⁻¹.

Various compositions (from 0 wt.% to 3 wt.% of LCC) of PE/LCC composites have been obtained by thermoplastic mixing in a Thermo PRISM TSE 16 TC twin-screw extruder at temperature range from 190 °C up to 235 °C.

Structure of the obtained PE/LCC compositions has been characterized by density, calorimetric and FTIR analyses. Density measurements have been performed at 20 °C by using Sartorius KB BA 100 electronic balance equipped with Sartorius YDK 01 density measurement kit. Measurements have been performed in air and ethyl alcohol as liquid testing media. Calorimetric measurements have been performed by using Mettler Toledo DSC 1/200W equipment. DSC experiments have been carried out in the temperature range from 25 °C to 300 °C at heating rate 10 °C/min. FTIR spectra have been obtained on a Smart Orbit ATR analyzer.

Stress-strain behaviour of PE/LCC composites has been determined by Zwick/Roell BDO FB020TN universal testing machine at 20 °C with the speed of the upper moving clamp 50 mm/min. 5 parallel specimens have tested.

Processing characteristics of PE/LCC blends have been determined in a stress sweep and frequency sweep modes by Reologica StressTech Nova rotational viscometer at 230 °C.

RESULTS AND DISCUSSION

Structure of self synthesized liquid crystal polyester copolymer (LCC) and selective polyethylene (PE) composites has been characterized by FTIR-ATR analysis. The region of 1800 cm⁻¹–500 cm⁻¹ was used for revealing the effect of LCC on the structure of the investigated PE composites. The respective spectra are shown in Fig. 1.

As one can see, spectra of PE/LCC composites contain expressed tensile vibrations of carbonyl groups C=O at 1733 cm⁻¹, vibrations of –CH groups in aromatic ring at 1604 cm⁻¹ and 1498 cm⁻¹, C–O tensile vibrations of ester groups at 1238 cm⁻¹ and 1189 cm⁻¹, –OH phenol group deformation vibrations at 1323 cm⁻¹ in the crystalline phase. Other characteristic vibrations, however, are not so strongly expressed.

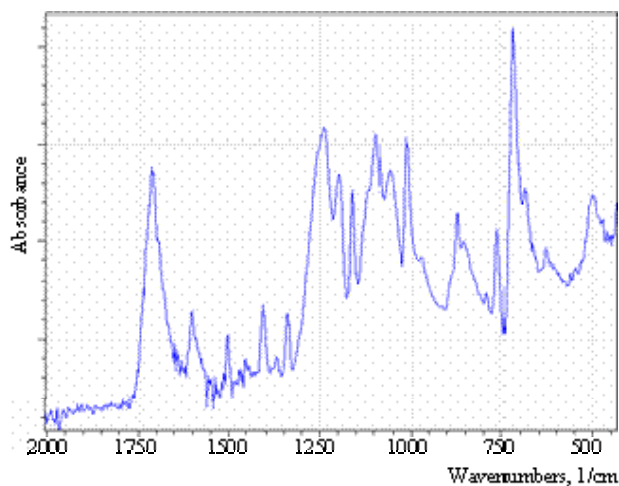
Structural perfectness of PE/LCC composites is expressed as a void content Ψ , which has been evaluated from the experimental density data:

$$\Psi = \frac{\rho_c - \rho_{\text{exp}}}{\rho_c} \cdot 100\%, \quad (1)$$

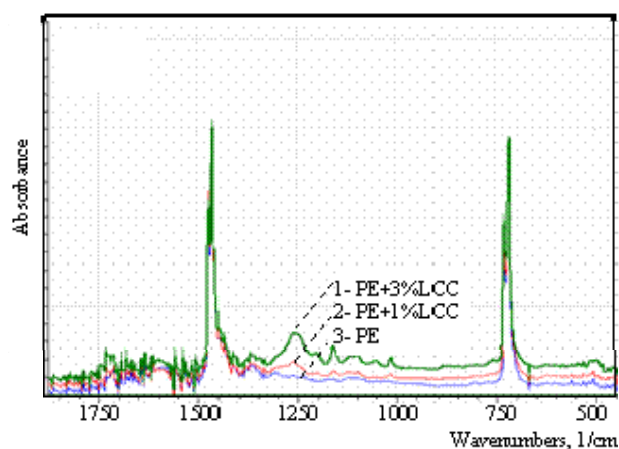
where ρ_c , ρ_{exp} are the theoretical and experimental density values. Theoretical densities of the investigated compositions have been calculated according to power law by using the classical equation:

$$\rho_c = \rho_m \cdot \varphi_m + \rho_f \cdot \varphi_f, \quad (2)$$

where ρ_m , ρ_f are the densities of the matrix (PE) and filler (LCC) respectively; φ_m , φ_f are the volumetric parts of the matrix (PE) and filler (LCC) respectively.



a



b

Fig. 1. Characteristic FTIR-ATR spectra of laboratory synthesized LCC (a), PE (b) and PE/LCC composites (b)

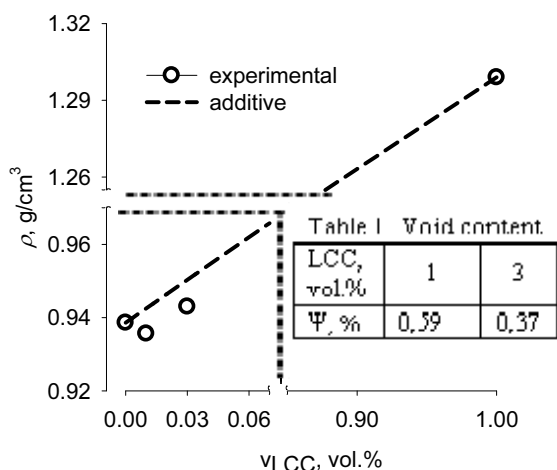
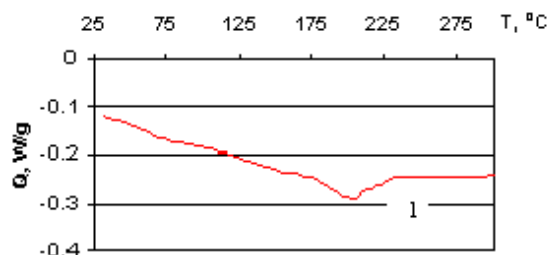


Fig. 2. Experimental (data points) and theoretical (dashed line) densities as well as respective void content (embedded Table 1) of the selected PE/LCC composites

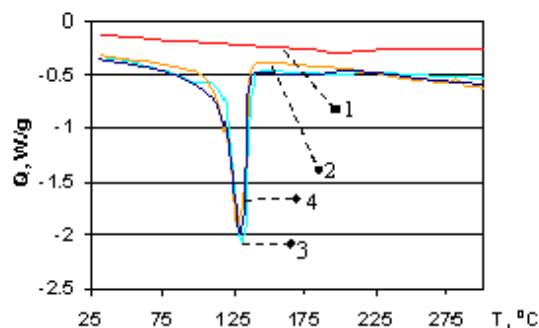
Experimental densities and respective void contents of the investigated composites are shown in Fig. 2. As one can see, densities of PE/LCC compositions increase with the growth of liquid crystalline modifier content. Void

content in the investigated PE composites has not been greater than 1 volumetric %.

Besides void content Ψ , another parameter, affecting structural perfectness and, hence exploitation properties of the material, is crystallization behaviour during manufacturing. Crystallized structure of the investigated PE/LCC compositions have been investigated by means of DSC experiments (see, Fig. 3. and Table 1).



a



b

Fig. 3. DSC scans of PE/LCC compositions: 1 – LCC; 2 – PE+LCC 1 %; 3 – PE+LCC 3 %; 4 – PE (denoted in wt. %)

Table 1. Calorimetric data of PE/LCC compositions*

LCC, wt. %	T_{on} , °C	T_{max} , °C	T_{off} , °C	ΔT , °C	ΔH , J/g, (χ , %)
0	55.5	129.1	141.0	85.5	139.8 (47.6)
1	66.7	127.9	141.3	74.6	145.0 (49.9)
3	78.4	131.2	143.0	64.6	142.2 (49.9)

* T_{on} ; T_{max} ; T_{off} – onset, maximal and offset temperatures of PE crystalline phase melting; ΔT – melting interval of PE crystalline phase; ΔH – melting enthalpy of PE crystalline phase; χ – crystallinity degree of PE (calculated by considering that melting enthalpy of a 100 percent crystalline polymer is 293.6 J/g)

From the respective DSC thermograms and the data, depicted in the Table 1, it is seen that addition of LCC to PE causes certain changes of the melting peak of the matrix polymer. Thus, shift of PE melting peak towards higher temperatures could testify about certain interaction between PE (melting temperature – 129.1 °C) and LCC (melting temperature – 202.6 °C). Simultaneously decrease

of the melting interval of PE could denote to the improved arrangement of PE crystallites. Both of these factors could play certain role in improvement of exploitation properties of PE/LCC blends.

Stress-strain data of PE compositions with LCC are shown in Fig. 4. As one can see, increase of LCC content causes growth of elastic modulus, yield stress and break stress of the investigated compositions by approximately 15 % and 30 % respectively. Simultaneously yield strains and ultimate strains of the compositions are decreased to certain extent, however, their decrement is not dramatic (for an example, break strain of PE/LCC 1 % composition is ca 200 %).

Rheological properties of PE/LCC compositions are summarized in Fig. 5. The effect of LCC content on rheological properties of the investigated PE/LCC compositions is evaluated at 230 °C, i.e. close to the offset melting temperature of LCC crystalline phase. As one can see in Fig. 5, viscosity curves of PE/LCC compositions, determined in both testing modes (stress amplitude sweep mode at 1 Hz frequency (characterizing linear viscoelasticity region) and frequency sweep mode (characterizing rheological behaviour closer to processing conditions)), are situated close to those of neat PE. These small changes, most probably are explained with considerable small amounts of LCC in the investigated composites. The viscosity curve of neat modifier as function of frequency, however, is situated well below the viscosity curve of PE as it is clearly depicted in Fig. 5, b. Thus it is expected that by increasing LCC content above 3 wt.%, viscosities of the compositions will decrease and their processing will be facilitated.

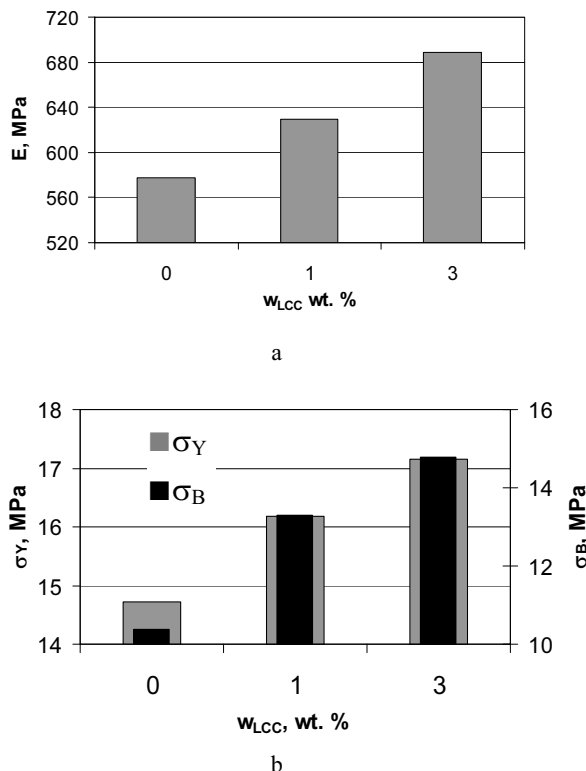


Fig. 4. Stress-strain characteristics of PE/LCC compositions: modulus of elasticity E (a), yield stress σ_Y and break stress σ_B (b) as functions of LCC weight content

CONCLUSIONS

Polyethylene (PE) and self-synthesized liquid crystal co-polyester (LCC) composites have been investigated at considerable small modifier contents. It has been observed that 1) elastic modulus E , yield stress σ_Y and break stress σ_B of the composites are already increased at LCC modifier content of 1 %; 2) by increasing LCC content up to 3 wt.%, growth of certain stress-strain characteristics of the investigated PE composites continues approximately at the same rate; 3) elastic modulus E , yield stress σ_Y and break stress σ_B of the composites at 3 wt.% of LCC are increased approximately by 15 % and 30 % respectively; 4) void content in the investigated PE/LCC compositions is not greater than 1 %; 5) addition of LCC improves arrangement of PE crystalline phase and causes certain shift in the melting peak of PE towards that of LCC modifier; 6) melt viscosities of PE/LCC blends change insignificantly with addition of LCC, most probably due to the small amounts of LCC modifier in the investigated compositions.

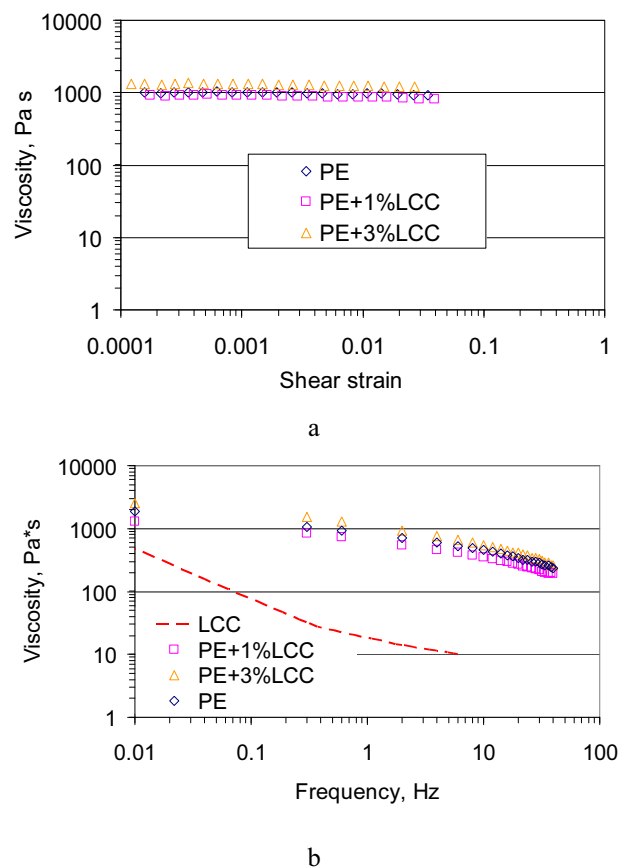


Fig. 5. Viscosity curves of PE/LCC compositions at 230 °C: a – stress amplitude sweep mode; b – frequency sweep mode

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