

Mechanical Properties of Injection-Molded Binary Blends of Polyethylene with Small Additions of a Liquid-Crystalline Polymer

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ABSTRACT: The results of the investigation of the mechanical properties of polyethylene (PE) blends with small (<3 wt %) additions of thermotropic liquid-crystalline polymers (LCPs) are reported. PE/LCP compositions with various LCP weight contents were obtained by thermoplastic mixing in a two-stage process. Short-term and long-term mechanical behavior of various PE/LCP compositions were analyzed. Data on the influence of LCP addition on the tensile elastic modulus [or Young's modulus (E)], stress at yield (σ_Y), stress at break (σ_B), strain at yield, strain at break, and deformation at long-term (1000-h) tensile creep were obtained. The experimental results of the investigation show that even small additions of LCP allowed considerable increases in E , σ_Y , σ_B , and creep resistance of PE. To sup-

port the experimental data, we mathematically analyzed the elastic properties of the materials by taking into account the effect of self-reinforcement due to the formation of extended LCP inclusions. The results of the theoretical analysis testify that LCP inclusions in the continuous PE matrix were elongated 5–10 times because of their orientation during the manufacturing of the test specimens. Analytical descriptions of the creep of the PE/LCP blends are also presented. It is demonstrated that the creep behavior of the PE/LCP blends could be sufficiently well described by power law. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3564–3568, 2011

Key words: creep; liquid-crystalline polymers (LCP); polyethylene (PE); strain; stress

INTRODUCTION

There are several purposes that are considered in the development of thermotropic liquid-crystalline polymer (LCP) modified thermoplastics. Improvements in the rheological, mechanical, and barrier properties and the dimensional and thermal stabilities have been revealed in LCP multicomponent mixtures with such polymers as polyethylene (PE),^{1–3} polypropylene,^{4–9} polystyrene,¹⁰ polycarbonate,^{9,11–15} poly(ethylene terephthalate),¹⁶ poly(butylene terephthalate),^{9,17,18} polyamide,^{19,20} poly(ether imide),^{21,22} poly(ether ether ketone),^{21,23} and elastomers.^{22,24} The main prerequisites for the effective reduction of viscosities, and hence, facilitated processing, are the existence of LCP inclusions in the nematic state with a critical concentration globally oriented in the flow direction.² The main reasons for enhanced barrier properties are, on the one hand, the dense packaging of the rigid LCP chains, and on the other hand, the continuity and lamellar shape of the LCP phase.³ The main cause of improved mechanical properties, in turn, is

formation of extended LCP fibrils in the matrix polymer. The so-called self-reinforcing effect is especially pronounced at extrusion and subsequent drawing of the compositions containing considerable amounts of LCPs (≤ 30 wt %).¹⁵ In fact, it is practically impossible to obtain completely isotropic specimens of LCPs because their manufacture is accompanied by inevitable shear-induced deformation, which leads to orientation of the labile liquid-crystalline (LC) structure and a substantial increase in the rigidity in the direction of extension. For example, in ref. 15, experimental data on the effect of stretching on the tensile elastic modulus or Young's modulus (E) of LCP of trademark Vectra B950 are reported. It is shown that with an increase in the stretch ratio (λ) from 1 to 3, E sharply grows from about 9 GPa to about 60 GPa, after which its growth slows down and, at a fivefold extension, asymptotically approaches 80 GPa. This work, however, was devoted to the investigation of the effect of small additions of LCPs on the short-term and long-term mechanical properties of PE.

EXPERIMENTAL

In this work, PE (Egypoptene MD 3804U, Egyptian European Co., Alexandria, Egypt), with a density of 0.938 g/cm³ and a melt index of 4.0 g/10 min, was

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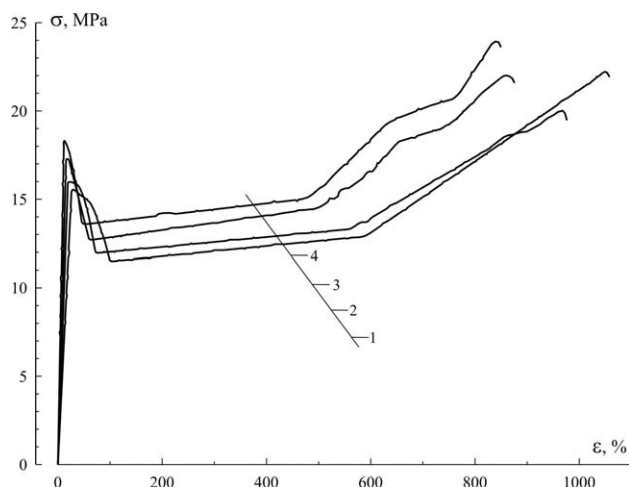


Figure 1 σ - ε diagrams of LCP/PE blends with different LCP contents: (1) 0, (2) 0.5, (3) 1, and (4) 3 wt %.

used as a matrix. A liquid-crystalline copolymer (Vectra B950, Ticona GmbH, Kelsterbach, Germany) was used as a modifier.

LCP/PE blends were obtained by mixing in a Banbury-type mixer followed by processing in a twin-screw extruder above LCP melting. The LCP content was in the range from 0 to 3 wt %.

Short-term tensile tests according to ISO 527 were performed with a Zwick/Roell BDO FB020TN universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany) at a temperature of 20°C. Dog-bone test specimens with a cross-sectional area of about 11 mm² and a gauge length of 25 mm were manufactured by injection molding. The distance between clamps was 50 mm; thus, at a deformation rate of 50 mm/min, the initial strain rate was about $1.6 \times 10^{-2} \text{ s}^{-1}$. Up to the formation of a neck, the deformations were measured with a Zwick no. 770 extensometer. Further extensions were determined according to changes in the distance between clamps.

The quasi-static E was found from the results of fast stepwise loading and unloading of specimens with a duration of the loading-unloading cycle of about 2 s. The ε assigned did not exceed 0.4%. The deformations of specimens in loading and unloading were approximately equal; that is, noticeable residual ε values were not observed. E was defined as the ratio between the stress (σ) applied and the ε measured.

One-thousand-hour tensile creep experiments were performed at constant 3-MPa static loads, which corresponded to strain (σ) values equal to 15–20% from the yield maxima of the investigated blends. The creep ε values were measured by a digital indicator MIB-Messzeuge GmbH, Spangenberg, Germany with an accuracy of 5 μm .

Calorimetric measurements were performed with Mettler Toledo DSC 1/200W equipment (Mettler-Toledo GmbH, Greifensee, Switzerland). Test objects with an average mass of 10 mg were taken from the

injection-molded dog-bone specimens. Tests were made in the temperature range from 25 to 300°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

σ - ε diagrams of the PE/LCP blends are shown in Figure 1, whereas corresponding σ - ε characteristics as functions of the LCP content are shown in Figure 2. It is demonstrated that with increasing LCP content in the blends, the σ - ε curves in the σ - ε coordinate system shifted to higher σ values. Thus, at an LCP content of 3 wt %, E and the stress at yield (σ_Y) of the composite were correspondingly 30 and 20% higher than those for neat PE. Although a considerable decrease (ca. two times) in the strain at yield (ε_Y) was observed, the addition of LCPs did not lead to the embrittlement of PE. Sharper peaks at yield were associated with the effect of LCP on the necking of the polymer. The narrowing of the neck in the presence of minor amounts of LCP, generally, is associated with the ease of its orientation and fibrillation; this facilitates a local increase in the compliance of the test specimens. Calorimetric investigations of the PE/LCP blends by DSC revealed that in the investigated LCP concentration interval no significant changes in the shape of the melting endotherms (on average, melting occurred within 70 and 140°C with melting maxima of ca 129°C) as well as crystallinity degrees (ca. 50%) of PE crystalline phase were determined.

Let us analyze the dependence of elastic modulus of the composite E on the weight content of LCP $W_f E(W_f)$ theoretically by using the known conception about the morphology of LCP-containing blends and composite models with anisometric filler particles. In the model, it is assumed that the elastic properties of the matrix do not change with the addition of LCP and that elongated LCP particles are uniformly dispersed in the

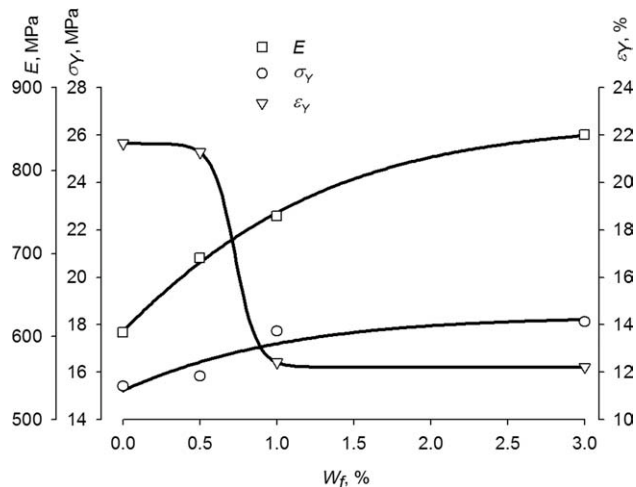


Figure 2 Experimental values of σ_Y , ε_Y , and E as functions of the LCP weight content W_f .

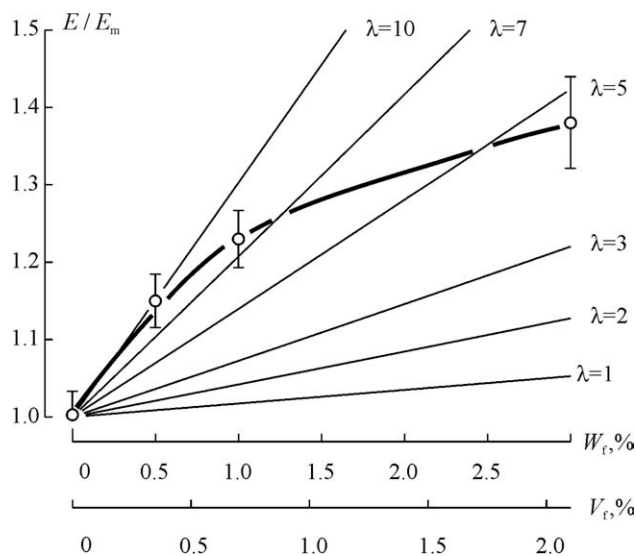


Figure 3 Relative modulus of elasticity E/E_m (E_m = elastic modulus of neat PE) of the LCP/PE blends as a function of the LCP content. The points indicate experimental data, and the lines indicate approximations calculated at different λ 's of the LCP inclusions.

material and are oriented in the axial direction of melt flow. Thus, a possible emergence of the effect of the migration of the LC component with the formation of the skin–core morphology is neglected.

E in the direction of orientation of anisometric filler particles, including short fibers, is usually determined by the Halpin–Tsai equation:²⁵

$$E = E_m \frac{1 + \xi \eta V_f}{1 - \eta V_f} \quad (1)$$

where η and ξ are coefficients, $\eta = \frac{E_f/E_m - 1}{E_f/E_m + \xi}$; $\xi = 2 \frac{l}{d}$; E is the elastic modulus of the composite; E_f and E_m are the elastic moduli of the inclusion and matrix, respectively; V_f is the volume fraction of inclusions; and l/d is the aspect ratio of the filler particles.

Because E of ordinary short fibers is practically independent of their length, in the calculations according to eq. (1), the quantity E_f is assumed to be constant and independent of l/d . This assumption is completely unacceptable in the case of LC particles. The deformation (extension) of such particles leads not only to an increase in it l/d but also to a considerable growth in its E_f . Therefore, in the case examined in this study, it was necessary to take into account the fact that E_f depended on l/d .

In our calculations, we employed the experimental data obtained in ref. 15 for relations between E of LCP of trademark Vectra B950 and λ . We assumed that the matrix and LC inclusions were strongly bonded together and that the volume ε values of the components at small tensile ε values of the composite were insignificant. Then, the relation between l/d and λ could be expressed by the following formula:

$$l/d = \lambda^{3/2} \quad (2)$$

where λ is the stretch ratio of the LC inclusions and is equal to the ratio of cross-sectional areas of a particle before and after its extension.

The dependence $E_f(l/d)$ was determined with eq. (2) taken into account, and the data on the effect of λ on E_f are presented in ref. 15. The values of the ratio between E of the composite and E_m , calculated according to eq. (1) with account of the dependence $E_f(l/d)$, are shown in Figure 3. In the calculations, E_m represents the experimentally detected E_m of neat PE ($E_m = 610$ MPa). The calculations were performed for several values of the λ of LCP particles in the interval from 1 to 10. The dots denote the ratios of the experimental values of E to E_m .

We should note that the calculation at $\lambda = 1$ corresponded to isometric ($l/d = 1$) isotropic LCP particles with an E equal to 9 GPa.¹⁵ With this assumption, the experimental values of the ratio E/E_m exceeded the theoretical ones considerably. Hence, the effect of self-reinforcement of the material, caused by the increased l/d of LCP particles and, which is of special importance, by the considerable increase in their E , must be taken into account.

As follows from the calculation results presented in Figure 3, an increase in λ at the same values of V_f led to a considerable growth in the relative E of the composite. The experimental data fell in the range of draw ratios from 5 to 10.

Figure 4 clearly illustrates the considerable influence of W_f and λ on the relative E of the composite; the change in the ratio E/E_m for W_f in the intervals from 0 to 5% and for λ 's from 1 to 10 is presented as a surface in spatial coordinates constructed according to calculated points for fixed values of W_f and λ .

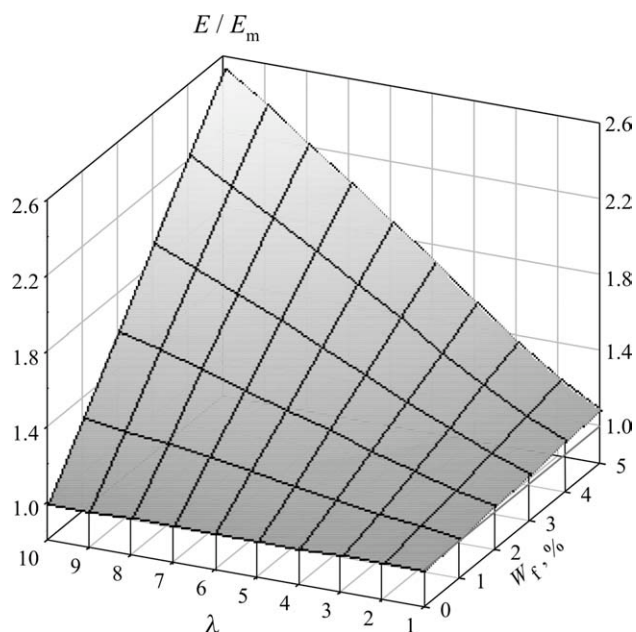


Figure 4 Surface of the relative elastic modulus E/E_m in the coordinates λ and LCP weight content W_f .

In opposite to short-term σ - ε behavior, the long-term creep effects on the exploitation characteristics of LCP containing thermoplastic composites were studied to a lesser extent, even though such materials have been intensively investigated for more than 20 years. However, in refs. 26 and 27, results for the semirigid LCP tested in creep at different temperature levels are reported. It has been shown²⁷ that below the glass-transition temperature and at loads below about 40% from the ultimate strength of LCPs, the polymer possesses an insignificantly small creep. The analysis of experimental results of the studies performed in refs. 26 and 27 also indicated that the effect of the temperature on the creep of the materials examined could be taken into account according to the method of temperature-time superposition.

The effect of LCPs on the creep behavior of thermoplastic polymers^{18,28} has also been reported. Published results on the long-term creep investigations (10,000 h) of PP modified with various amounts of liquid-crystalline additives [poly(ethylene terephthalate)/*p*-hydroxybenzoic acid]²⁸ show that certain LCP additions allow considerable improvements in the creep resistance of the polymer. An analogous effect was also observed for the investigated LCP/PE blends, as demonstrated in Figure 5. As one can see, after the duration of tensile creep (at 3 MPa) for 1000 h, ε of the composite containing 3 wt % LCP was 1.3 times smaller than that of neat PE. It seemed reasonable to verify the possibility of a compact (with a small number of coefficients) approximation of the experimental data by the so-called power law of creep:

$$\varepsilon(t) = \varepsilon_0 + \varepsilon_c t^n \quad (3)$$

where ε_0 is the instantaneous strain and ε_c and n are coefficients. The approach is described more in detail in ref. 29. Besides, in our previous investigation, it was found that eq. (3) could be used to describe not only the creep of pure polymers but also that of various binary/multicomponent systems, such as polymer blends^{30,31} and highly filled polyester composites.³²

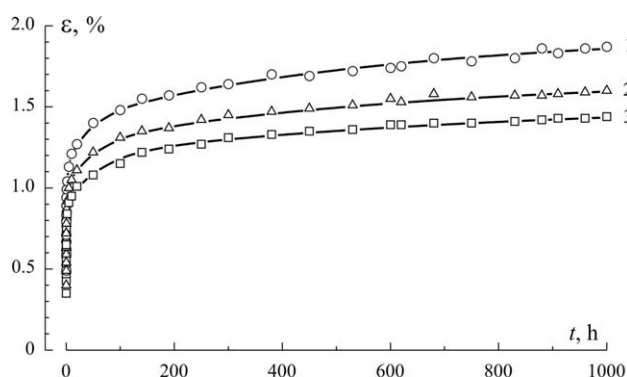


Figure 5 Creep curves $\varepsilon(t)$ of the LCP/PE composites at various LCP concentrations: (1) 0, (2) 1, and (3) 3 wt %.

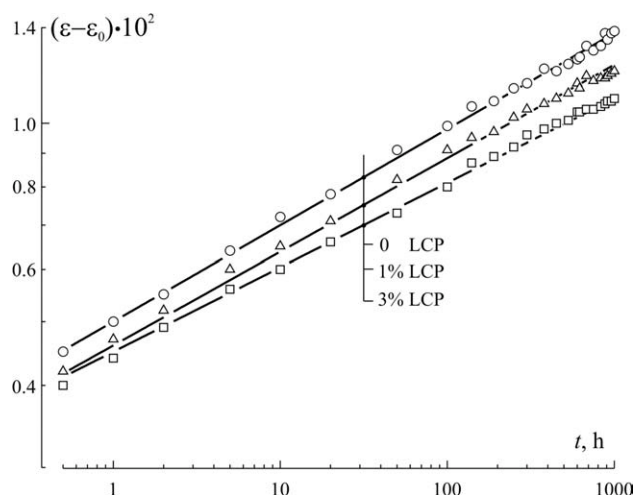


Figure 6 Creep ε values (total creep ε minus ε_0) of the LCP/PE blends in the logarithmic coordinates. The points indicate experimental data, and the lines indicate approximations according to eq. (4).

Expression (3) can be written as

$$\log(\varepsilon - \varepsilon_0) = \log \varepsilon_c + n \log t \quad (4)$$

which is the equation of a straight line with an inclination n in the axes $\log(\varepsilon - \varepsilon_0)$ and $\log t$. The experimental creep data in these axes are shown as points in Figure 6. It should be noted that the time t in eqs. (3) and (4) is regarded as a nondimensional ratio between the current time and a unit of time, assumed to be 1 h in our calculations. The straight lines in Figure 6 were drawn by the method of least squares. The average relative approximation error did not exceed 4%. As one can see, the experimental points were really arranged along straight lines.

CONCLUSIONS

In the current research, the effects of small additions (≤ 3 wt %) of LCP on the short-term and long-term (creep up to 1000 h) tensile properties of PE are revealed. Experimental results of the investigation show that even small additions of LCP allowed considerable increases in E , σ_Y , ultimate σ , and creep resistance of PE. Theoretical analysis, carried out in the framework of this investigation, allowed us to assume that LCP inclusions in the continuous PE matrix were elongated 5–10 times because of their orientation during the manufacturing of the test specimens. Besides, theoretical analysis showed that the creep of the investigated LCP/PE blends could be sufficiently well described by power law.

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