

# Effect of a Filler on the Rheological and Mechanical Properties of the Liquid-Crystalline Polyester–Poly(methyl methacrylate) Blends

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**ABSTRACT:** The rheological and mechanical properties of the blends of liquid-crystalline polyester (LCP) and poly(methyl methacrylate) (PMMA) filled with aluminum borate whiskers have been studied. It was established the combined action of reinforcing LCP and filler onto the property of PMMA matrix leads to marked reinforcing of PMMA. At 10% of filler and 30% of LCP, the tensile strength of PMMA increases by 30% and elasticity modulus by 110%, the processability being no worse. The viscosity of the blend PMMA + 30% LCP + 10% filler practically is the same as the PMMA melt viscosity at 220°C. With increasing concentration of LCP up to 30%, the filler effect in binary matrix becomes more essential. The possible reason is the preferential adsorption of LCP at the filler interface (surface segregation) and additional ordering of LCP near the surface, possible, due to additional stretching of nematic phase in the convergent flow zone. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 993–999, 2000

**Key words:** liquid-crystalline polymer; filled blend; whiskers

## INTRODUCTION

The ability of liquid-crystalline polymers (LCP) to change their structure and physical and mechanical properties by phase transitions is widely used for advanced composite materials. A very interesting behavior of two-phase blends of LCP and thermoplastics has been observed in many works (see, for example, ref. 1). It was found<sup>2</sup> that at the concentration of LCP in the blends on the order 3–30% promotes a sharp decrease in viscosity (especially by capillary flow) of the blend that becomes practically equal to that one for LCP. According to the current point of view, the effect of diminishing viscosity is determined by anisotropy of viscosity of LCP, their migration to the channel

wall, and possible interfacial slippage.<sup>3</sup> The heterogeneous phase morphology of the blends based on LCP not only diminishes the viscosity of a blend, but improves the mechanical properties of extruded materials. It was supposed<sup>1</sup> that the mechanism of such improvement consists of the formation of so-called self-reinforced composites, i.e., materials where fibrils of LCP reinforce the isotropic polymeric matrix.

From the general conclusions<sup>4–6</sup> as to the changes of the structure and rheological and mechanical properties of filled thermoplastics and elastomers, one can suppose that introduction of fillers into the LCP matrix may lead not only to improving properties but to diminishing the cost. In the last several years we have done some investigations of the rheological and mechanical properties of filled LCP<sup>7,8</sup> and their blends with thermoplastics.<sup>9–11</sup> The traditional particulate fillers (carbon black, silica, talc) and fibrous (glass fiber) were used. The main result of these inves-

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tigations consists of establishing the fact of diminishing the viscosity of LCP at a low degree of loading for particulate fillers and of increasing moduli of solid extrudates. For the LCP-polypropylene blend it was found that by using the short-cut glass fibers as a filler, a marked reinforcing of the materials occurs at 30% content of LCP, when by extrusion the fiber forming proceeds.<sup>11</sup>

A great possibility to obtain the compositions of high performance may be reached by using the thread-like monocrystals-whiskers as a filler. Whiskers possess the mechanical tensile strength close to the strength of the chemical bonds between atoms.<sup>12</sup> For example, whiskers of silicon carbide have the tensile strength more than 30 GPa and elasticity modulus more than 690 GPa. The perfection of the inner structure and the surface of the whiskers determine their extremely low brittleness as compared with glass fibers.

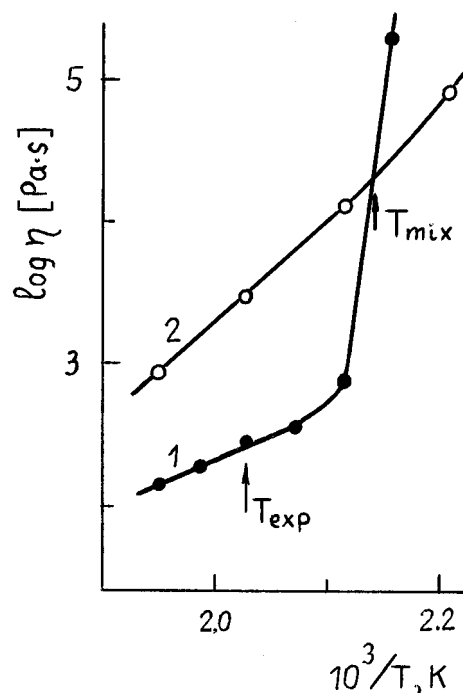
The present paper develops some concepts on the rheological behavior of LCP-thermoplast blends. Our aim was to establish the effect of the thread-like monocrystals-aluminum borate whiskers on the rheological and mechanical properties of blends. The rheological characteristics, as distinct from preceding works, were investigated both at the capillary flow and in the regime of shear oscillation.

## EXPERIMENTAL

We have used as an LCP the copolyester of poly(ethylene terephthalate) (PETP) and *p*-oxybenzoic acid (ratio 40/60,  $\eta_{sp} = 0.51$  in trifluoroacetic acid). The melting point of copolyester was 180°C. This LCP has two main relaxation transitions  $T_{g1} = 70^\circ\text{C}$  and  $T_{g2} = 160^\circ\text{C}$  that correspond to the large scale mobility of the chain fragments enriched correspondingly in PETP and oxybenzoic acid (OBA). The blends of this LCP with poly(methyl methacrylate) (PMMA) ( $M_w = 91,300$  and  $M_n = 30,800$ ) were used.

As a filler, the alumino-borate whiskers  $W_{ab}$  were used:  $(\text{Al}_2\text{O}_3)_9 (\text{B}_2\text{O}_3)_2$  (Shi Koku Chemical Corp.). Whiskers are monocrystals with dimensions  $d = 0.5-1$ ,  $l = 10-30$  mcm, density  $W_{ab} = 2.93 \text{ g/cm}^3$ , specific surface  $S_{sp} = 2.5 \text{ m}^2/\text{g}$ . The degree of loading the blends and its components was taken up to 20% by weight.

Before mixing, PMMA was dried under vacuum at 100°C and  $W_{ab}$  and LCP at 120°C for one day. The mixing of components in presence and absence of a filler was performed in micromixer of



**Figure 1** Temperature dependence of viscosity of LCP (1) and PMMA (2) at  $\tau = 1.51 \cdot 10^4$  Pa.

rotator-plunger type (the gap between rotor and inner cylinder 0.25 mm, minimal charging 3.5 g, shear rate in the gap  $500 \text{ s}^{-1}$ ) at 194°C. The choice of this temperature was dictated by the fact that at this temperature LCP and PMMA have the same viscosity, which is of importance in obtaining uniform blend and filler distribution. Figure 1 shows the temperature dependencies of viscosity of PMMA and LCP in Arrhenius coordinates. The arrows indicate the temperature of mixing (194°C) and of experiment (220°C).

The rheological measurements were done using capillary microviscosimeter MV-2<sup>13</sup> and using rheometer PIRSP-03<sup>14</sup> at harmonic small amplitude vibrations (the region of frequencies from  $10^{-13}$  to  $10 \text{ s}^{-1}$ ). The mechanical characteristics of solid extrudates done using the MV-2 device were measured by extension using dynamometer.

## RESULTS AND DISCUSSION

### Rheological Properties

#### *Rheological Characteristics at Capillary Flow*

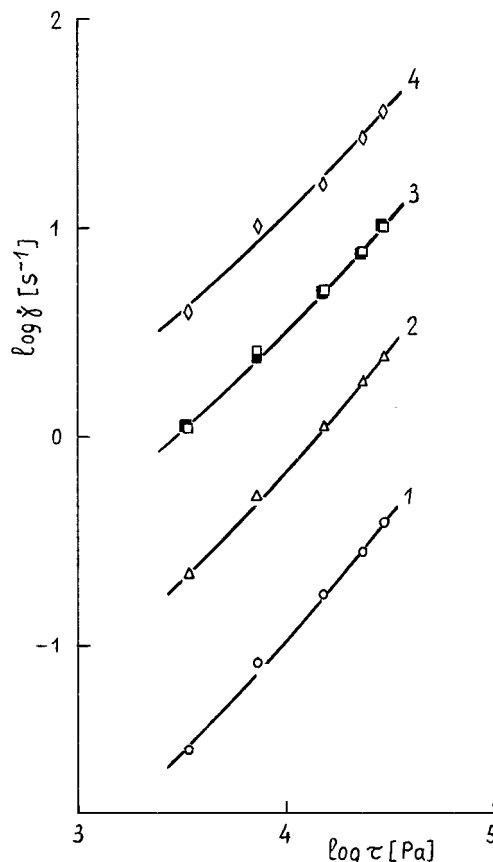
The dependence of  $\lg \eta(1/T)$  (Fig.1) for LCP has two temperature regions below and above 200°C. In these regions the activation energies of viscous

flow  $E$  are sharply different: at  $T < 200^\circ\text{C}$   $E_{\text{LCP}} = 1000$  kJ/mol, whereas at  $210\text{--}240^\circ\text{C}$ ,  $E_{\text{LCP}} = 65$  kJ/mol. In the temperature region  $200\text{--}240^\circ\text{C}$ ,  $E_{\text{PMMA}} = 135$  kJ/mol. To explain the temperature dependence of viscosity of LCP, one should have in mind that macromolecules of LCP contain long block sequences of OBA. In LCP there are observed, because of this, at least two relaxation transitions at temperatures  $70$  and  $160^\circ\text{C}$ , melting of the main part of crystallites at  $180^\circ\text{C}$  and melting of crystallites enriched in OBA block at temperatures above  $210^\circ\text{C}$ . From literature data<sup>15–18</sup> and Figure 1, one can suppose that in spite of the softening of LCP at  $180^\circ\text{C}$ , there are preserved some crystallites formed by OBA sequences that have their melting point above  $210^\circ\text{C}$ . Therefore, LCP at temperatures below  $200^\circ\text{C}$  has two-phase structure with high viscosity. Above  $210^\circ\text{C}$  in melt, the homogeneous nematic structure appears and the viscosity of such a homogeneous melt is between  $100$  and  $400$  Pa s in the temperature interval  $210\text{--}240^\circ\text{C}$ .

Figure 2 presents the dependencies of the shear rate  $\dot{\gamma}$  on the shear stress  $\tau$  in double logarithmic coordinates for PMMA at various temperatures. Dark points on the flow curve, relating to the temperature  $220^\circ\text{C}$ , were obtained for PMMA run through the mixer at the conditions mentioned above. It is seen that rheological characteristics of the initial PMMA do not change after the shear deformation in the working unit of the micromixer. The same relates to the initial LCP.

Figure 3 shows the flow curves for LCP, PMMA, and their blends at  $220^\circ\text{C}$ . It is seen the curves for LCP and PMMA are sharply different: the curve  $\lg \dot{\gamma}$  ( $\lg \tau$ ) for LCP has much higher slope as compared with PMMA. The shape of the flow curve for LCP implies its viscoplastic behavior is due to existence of the yield point. The latter is related<sup>1,19</sup> to the presence in the nonoriented LCP specimen of the disclination network and breakage lines of optical homogeneity of the medium, which determine the resistance to uniform plastic deformation of the anisotropic medium. Rheological behavior of PMMA at given ( $\dot{\gamma}$ ,  $\tau$ , and  $T$  are characterized only by the low viscosity anomaly (Figs. 2 and 3).

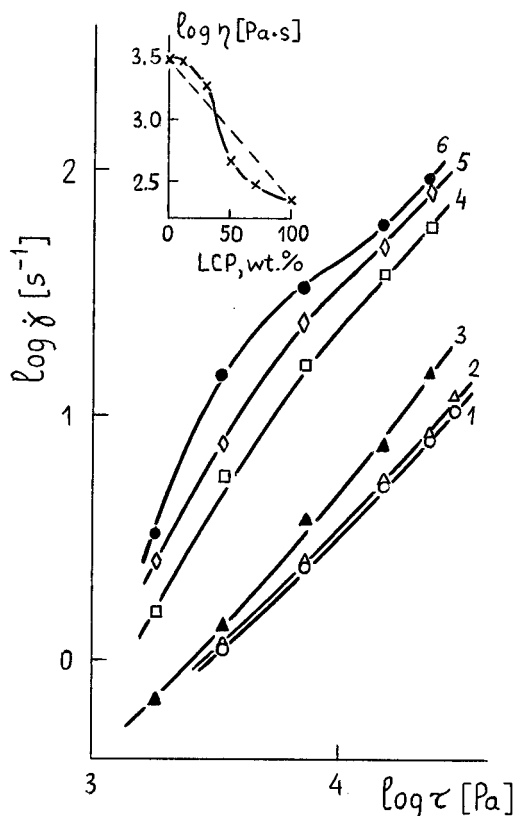
Adding 10% of LCP to PMMA does not change the shape of the flow curve as compared with pure PMMA, the latter being only slightly shifted to the region of higher shear rates. Subsequent increasing of the LCP concentration in the blend (30%) leads to the marked increase of the  $\lg \dot{\gamma}$  ( $\lg$



**Figure 2** Flow curves at  $180^\circ\text{C}$  (1),  $200^\circ\text{C}$  (2),  $220^\circ\text{C}$  (3), and  $240^\circ\text{C}$  (4). Dark squares relate to PMMA run through the mixer.

$\tau$ ) slope, i.e., to increasing viscosity anomaly. At LCP concentrations 50 and 70% the yield point appears for the blend, being possible connected with the phase inversion. At these LCP concentrations the continuous phase is nematic melt of LCP, whose viscoelastic behavior is determined by the existence of the yield point.

The dependence of the viscosity on the blend composition at the constant shear stress is shown in the upper left part of Figure 3. Such a diagram is typical of two-phase polymeric blends. Because at the given temperature  $\eta_{\text{LCP}} < \eta_{\text{PMMA}}$ , the addition of 10% LCP to PMMA leads to the marked drop in viscosity. However, this fact is not the only reason for decreasing of the blend viscosity. We have established that the specific fiber forming of the dispersed LCP phase in the PMMA matrix (concentration region  $10\text{--}50\%$ ), proceeding by capillary flow, occurs at temperatures no lower than  $220^\circ\text{C}$ , whereas at lower temperatures (below  $210^\circ\text{C}$ ) such a phenomenon is not observed. As noted above, the fiber forming charac-



**Figure 3** Flow curves for PMMA (1) and LCP (6) and their blends: 9/1 (2), 7/3 (3), 5/5 (4), and 3/7 (5) at 220°C. Dependence of the viscosity on the composition at  $\tau = 7.24 \cdot 10^3$  Pa.

teristics of dispersed LCP diminish the blend viscosity. It is worth noting that for the PMMA/LCP = 7/3 blend in absence of a filler, a distinct swelling of extrudate takes place, whereas in the whisker presence the swelling is practically suppressed. This effect seems to be connected with more fine dispersion of the LCP phase in the whisker presence. Similar results have been obtained for the ternary mixture polypropylene-LCP-glass fiber.<sup>11</sup>

Consider now the rheological behavior by capillary flow for filled blends. Figure 4 shows the flow curves for filled LCP (A), PMMA (B), and 7/3 PMMA/LCP blend (C). The same figure shows the dependence of the relative viscosity on concentration of a filler for LCP/ $W_{ab}$  and PMMA/ $W_{ab}$  mixtures. From the data we get the following:

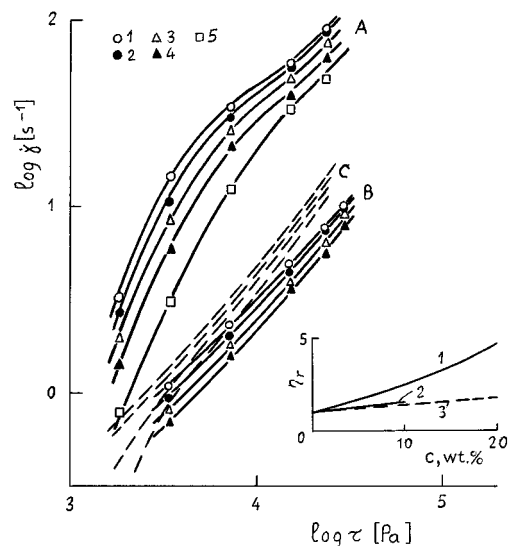
1. Filler does not affect the flow curves, which only becomes convergent at high shear stresses.
2. Concentration dependence of the viscosity

for PMMA and binary mixture PMMA/LCP = 7/3 is a weakly increasing function, whereas for LCP the same dependence is stronger at low shear stresses. This shows that the formation of the structure is due to filler-particle interactions in the nematic melt.

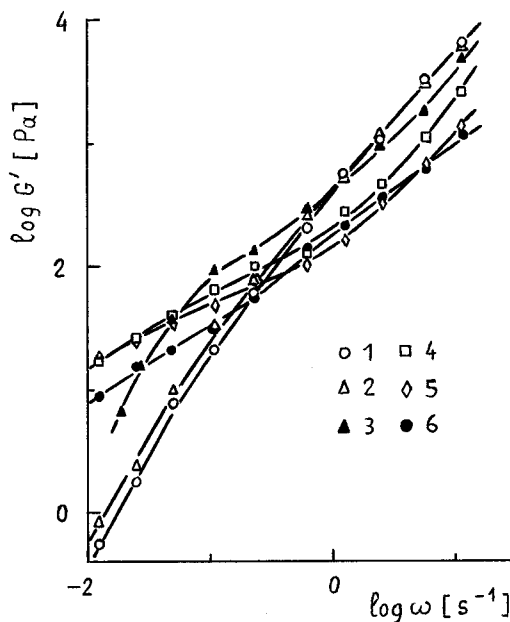
3. The viscosity of the PMMA/LCP = 7/3 blend in presence of 10%  $W_{ab}$  practically does not differ from the viscosity of PMMA at  $\tau = 7200$  Pa and is lower at more high shear stresses.

#### Rheological Characteristics at Harmonic Vibrations

Consider now the results of measurements at conditions of harmonic vibrations at low amplitude of deformation. Figures 5-7 give the corresponding values of the elasticity modulus  $G'$ , loss modulus  $G''$ , and dynamic viscosity  $\eta'$  as a function of the circular frequency  $\omega$  for PMMA, LCP, and their blends. From these data it is seen that the relaxation behavior of the isotropic melt of PMMA and nematic melt of LCP is very different, especially in the low frequencies region. At this condition the exponents in dependencies  $G' \sim \omega^a$  and  $G'' \sim \omega^b$  for LCP are lower as compared with PMMA. For PMMA with flexible polymeric chains  $a = 2$ ,  $b = 1$ , in correspondence with theoretical values.<sup>6</sup> At the same time,

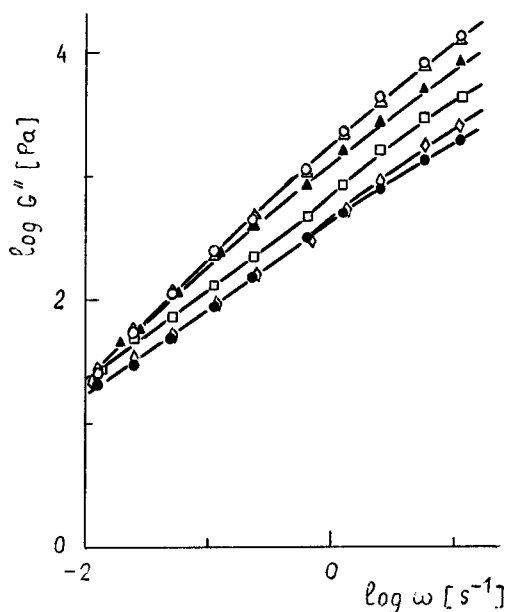


**Figure 4** Flow curves for filled LCP (A), PMMA (B), and 7/3 blend (C). The  $W_{ab}$  content in the blends: 0 (1), 2 (2), 5 (3), 10 (4), and 20 (5) % wt.  $T = 220^\circ\text{C}$ . Dependence of the relative viscosity on filler concentration for LCP (1,3) and PMMA (2,3) at  $\tau = 3.39 \cdot 10^3$  (1, 2) and  $2.34 \cdot 10^4$  Pa (3).

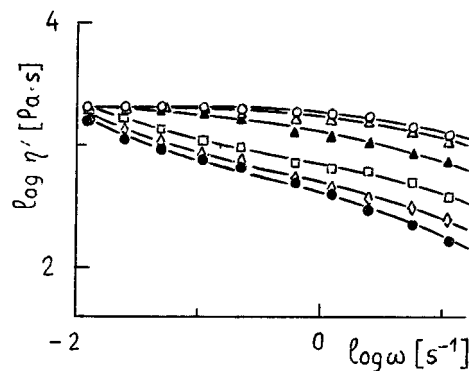


**Figure 5** Frequency dependence of dynamic elasticity modulus  $G'$  for PMMA (1), LCP (6) and blends 9/1 (2), 7/3 (3), 5/5 (4), 3/7, and (5) at 220°C.

for LCP  $a = b = 0.7$ , these exponents being close to that one predicted for anisotropic systems, for which  $a = b = 1$ .<sup>1</sup> For PMMA/LCP blends exponents are close to the value for the component that forms continuous medium.



**Figure 6** Frequency dependence of dynamic loss modulus  $G''$  for PMMA, LCP, and blends. For designation, see Figure 5.

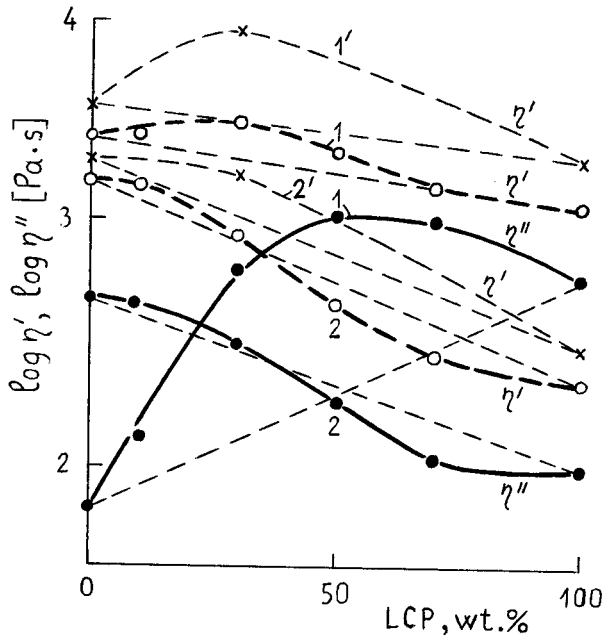


**Figure 7** Frequency dependence of dynamic viscosity for PMMA, LCP, and blends. For designation, see Figure 5.

As follows from Figure 7, the dynamic viscosity  $\eta'$  for PMMA in the region of low frequencies does not depend on  $\omega$  (linear region of viscoelasticity). By increasing frequencies the value  $\eta'$  diminishes regularly. The same behavior is typical of the blends where PMMA forms a continuous medium (LCP content 10–30%). The same is valid in the region of high frequencies for the LCP and the blends where LCP is the continuous phase (LCP content 50 and 70%). In this case the slope of the curve  $\eta'(\omega)$  is higher. However, in the low frequency region the existence of the yield point in LCP exerts its effect: function  $\eta'(\omega)$  is increasing function with diminishing frequency.

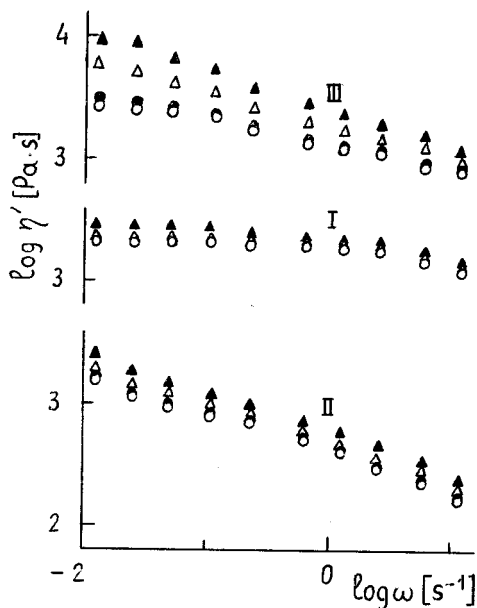
Figure 8 presents the dependencies of the real [ $\eta' = (G''/\omega - \text{dynamic viscosity})$ ] and imaginary [ $\eta'' = G'/\omega - \text{elasticity}$ ] parts of the complex dynamic viscosity  $\eta^*$  on the blend composition at high and low frequencies. The composition dependence is similar to the same dependence of the static viscosity  $\eta$  (Fig. 3). The same is valid for the dependence of  $\eta''$  on composition at high frequencies. However, at low frequencies the marked positive deviation of experimental values of  $\eta''$  from additive ones takes place. Presently we cannot explain this fact.

For filled PMMA the weak dependence of the dynamic viscosity on  $W_{ab}$  concentration is typical (Fig. 9). The same dependence is more pronounced for LCP. The addition of 10%  $W_{ab}$  does not change the shape of the curve  $\eta'(\omega)$ —the dependencies for filled and unfilled LCP are similar. This result shows that the filler does not form the continuous phase in nematic LCP melt and at low frequencies plays a role of usual thickener. At the same time it is possible that

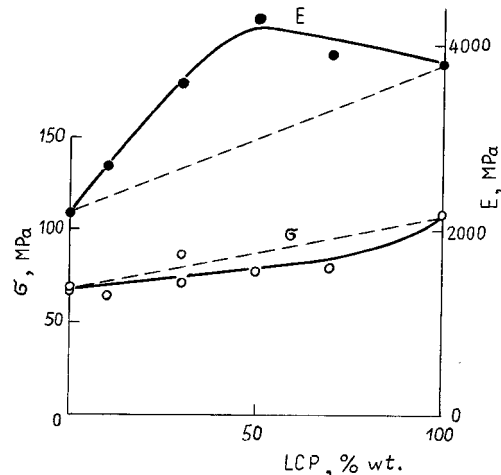


**Figure 8** Dependence of the real (viscosity)  $\eta'$  (dotted thick lines) and imaginary (elasticity)  $\eta''$  (solid lines) parts of complex viscosity on composition of the blends at various frequencies:  $\log \omega = 1.6$  (1) and 0.8 (2). Curves 1' and 2' relate to the blend containing 10%  $W_{ab}$ .

the low deformation amplitude does not “feel” the existence of the structural network formed by filler particles, as observed by capillary flow.



**Figure 9** Frequency dependence of dynamic viscosity for filled systems: PMMA (I), LCP (II), and 7/3 blend (III). For designation, see Figure 4.

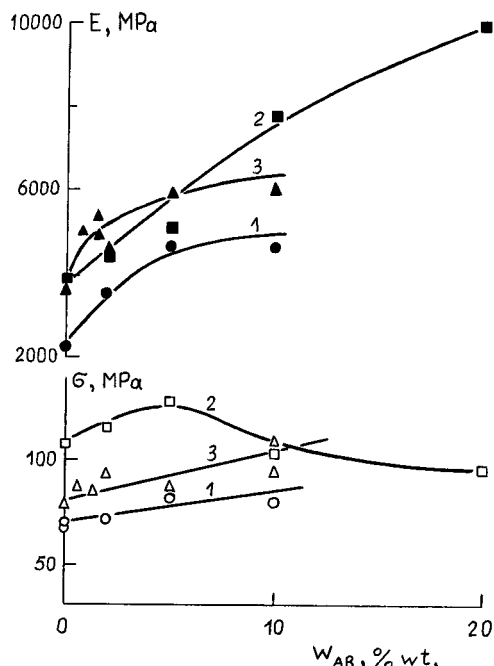


**Figure 10** Dependence of the tensile strength  $\sigma$  and initial elasticity modulus  $E$  at elongation on the blend composition.

The rather strong dependence of the dynamic viscosity on the filler concentration for PMMA/LCP = 7/3 blend seems to be unexpected (Fig. 9, III). Figure 8 shows (thin dotted line) the dependence of  $\eta'$  on composition for this blend in the presence of 10%  $W_{ab}$ . The marked positive deviation of  $\eta'$  from additivity is seen (compare with the curve 1 for unfilled blend curve 1'). It is possible this result reflects the enhancement of the interaction between blend components in the presence of whiskers if to assume that the positive deviation is a sign of increasing interfacial interaction (compatibilization<sup>20</sup>). With increasing frequency, the degree of positive deviation from additivity diminishes. The same conclusion about the influence of a particulate filler (carbon black) on the interfacial interaction between components was made for the LCP–poly-sulfone blend.<sup>9</sup>

### Mechanical Properties of Extrudates

Figure 10 shows the composition dependence of the tensile strength  $\sigma$  and initial modulus of elasticity  $E$  at elongation for solid extrudates obtained by capillary flow at 220°C. The dependence of  $\sigma$  on the blend composition is the slightly increasing function that almost does not deviate from additivity. This allows one to predict the tensile strength of solid extrudates formed at conditions of convergent flow from the values for pure components ( $\sigma_{\text{PMMA}} = 70 \text{ MPa}$ ,  $\sigma_{\text{LCP}} = 110 \text{ MPa}$ ). The elasticity modulus increases with increasing LCP content in PMMA matrix up to 50% and then diminishes to values for LCP. Generally, the experimental values of the blends are above addi-



**Figure 11** Dependence of the tensile strength  $\sigma$  and initial modulus  $E$  at elongation on the filler content for PMMA (1), LCP (2), and 7/3 blend (3).

tive ones. From what has been said in preceding sections it may be suggested that fibrillization of isotropic PMMA melt due to LCP presence exerts the reinforcing effect. In this relation this system differs from the polypropylene–LCP blends,<sup>11</sup> probably due to stronger interactions between PMMA and LCP and higher adhesion strength at the interface between components. Really, the strength of adhesion bonds between polypropylene and LCP is 1.25 MPa,<sup>11</sup> whereas between PMMA and LCP 3.1 MPa (unpublished data).

Figure 11 gives the dependencies of the mechanical characteristics of solid extrudates on the whisker concentration for pure components and PMMA/LCP blend 7/3. It is seen that the tensile strength of PMMA linearly increases with  $W_{ab}$  concentration. The same is valid for the 7/3 blend. For filled LCP, first increasing up to  $W_{ab}$  5% and then diminishing, this effect resembles the behavior of the LCP–carbon black composition<sup>18</sup> and usual increases in stiffness of isotropic polymeric medium. The changes of the elasticity modulus proceeds in a similar way, with increasing filler concentration in pure PMMA and PMMA/LCP blends.  $E$  first increases up to 5%  $W_{ab}$  and then its value does not change. A twofold increasing modulus is observed for LCP at  $W_{ab} = 20\%$ .

Thus, combination of both LCP and whiskers as reinforcing agents leads to marked reinforcing

of PMMA with preservation of its processability. The reason for this effect seems to be the change in the interaction between filler and the blend components, and preferential wetting of the filler surface by LCP (surface segregation). The additional ordering of LCP due to additional stretching of nematic phase in the convergent flow zone seems to be probable.

## REFERENCES

1. Kulichikhin, V. G. *Liquid Crystalline Polymers*; Khimia: Moscow, 1988; chap 9, pp 331–371.
2. Kulichikhin, V. G.; Vasiljeva, O. V.; Litvinov, I. A.; Parsamyan, I. L.; Plate, N. A. *Dokl AN USSR* 1989, 309, 1161–1164.
3. Hawksworth, M.; Hull, J. B.; Collyer, A. A. *Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends*; Ontario, 1993; p 65.
4. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker, INC, NY, 1974.
5. Lipatov, Yu. S. *Physical Chemistry of Filled Polymers*; British Library—RARPA: London, 1979.
6. Vinogradov, G. V.; Malkin, A. Ya. *Rheology of Polymers*; Khimia: Moscow, 1980.
7. Shumsky, V. F.; Dreval, V. E.; Getmanchuk, I. P.; Parsamyan, I. L.; Lipatov, Yu. S.; Kulichikhin, V. G. *Vysokomol Soed* 1990, B32, 739–742.
8. Shumsky, V. F.; Getmanchuk, I. P.; Parsamyan, I. L.; Lipatov, Yu. S.; Kulichikhin, V. G. *Polym Sci USSR* 1992, 34, 56–61.
9. Shumsky, V. F.; Lipatov, Yu. S.; Kulichikhin, V. G.; Getmanchuk, I. P. *Rheol Acta* 1993, 32, 352–360.
10. Getmanchuk, I. P.; Shumsky, V. F.; Lipatov, Yu. S.; Parsamyan, I. L.; Kulichikhin, V. G. *Vysokomol Soed* 1997, A39, 306–311.
11. Kulichikhin, V. G.; Parsamyan, I. L.; Lipatov, Yu. S.; Shumsky, V. F.; Getmanchuk, I. P.; Babich, V. F.; Postema, A. R. *Polym Eng Sci* 1997, 37, 1314–1321.
12. Katz, H. S.; Milewsky, V., Eds. *Handbook of Fillers and Reinforcements for Plastics*; Van Nostrand Reinhold Company: New York, 1978.
13. Konyukh, I. V.; Vinogradov, G. V.; Konstantinov, A. A. *Plast Massy* 1963, N10, 45–49.
14. Vinogradov, G. V.; Malkin, A. Ya.; Plotnikova, E. P.; et al. *Vysokomol Soed* 1978, A20, 226–230.
15. Blizard, K. G.; Baird, D. G. *Polym Eng Sci* 1987, 27, 653–662.
16. Sugigama, H.; Lewis, D. N.; White, I. L.; Fellers, J. F. *J Appl Polym Sci* 1985, 30, 2329–2341.
17. Viney, C.; Vindle, A. H. *J Mat Sci* 1982, 17, 2661–2670.
18. Jacson, W. J.; Kuhfuss, H. F. *J Polym Sci Polym Chem Ed* 1976, 14, 2043–2058.
19. Kulichikhin, V. G.; Bilibin, A. Yu.; Antipode, E. M.; et al. *Vysokomol Soed* 1990, A32, 70–76.
20. Lipatov, Yu. S. *Dokl AN USSR* 1991, 317, 673–679.