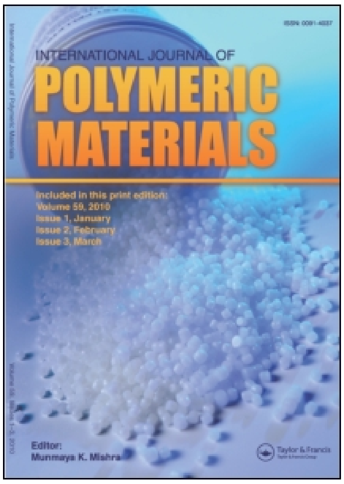

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Glass Transition Temperature, Compatibility and Viscosity of Poly(methyl metacrylate) Blended with Homo-or Copolymers of Alkyl Metacrylates

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Glass Transition Temperature, Compatibility and Viscosity of Poly(methyl metacrylate) Blended with Homo- or Copolymers of Alkyl Metacrylates

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Investigation of glass transition temperature and viscosity of binary mixtures of poly(methyl metacrylate) with statistic copolymers of methyl metacrylate and ethyl, butyl or octyl metacrylates as well as mixtures of poly(methyl metacrylate) with poly(ethyl, poly(butyl or poly(octyl metacrylates) has been carried out. The regions of one- and two-phase states of the above-mentioned mixtures were found from the glass transition temperature date. It has been shown that the mixtures of poly(methyl metacrylate) with copolymers of methyl metacrylate in combination with ethyl metacrylate are capable of forming one-phase systems throughout the whole range of the mixture compositions when extensively varying the copolymers compositions. The transition to copolymers of methyl metacrylate involving butyl and especially octyl metacrylates leads to a sharp narrowing of the range of the composition of their mixtures with poly(methyl metacrylate) in which they form one-phase-systems. We have established dependences of compatability boundaries of the polymers under investigation on their solubility parameters. It has also been shown that the viscosities of the one-phase systems under study vary with mixture concentrations according to the simplest additivity rule of viscosity logarithm. The transition to a two-phase mixtures leads in most cases to a negative divergence from the rule. A dramatic increase in their viscosity can take place in the narrow composition region on transition from a one-phase to a two-phase state.

KEY WORDS Polymetacrylate, polymer mixtures, compatibility, glass transition temperature, viscosity.

1. INTRODUCTION

One of the principle means of modifying polymer material properties is making up polymer mixtures. In this case, compatibility of the mixture components is of

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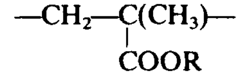
† Deceased.

great importance. One of the well-known ways of estimating compatibility lies through the investigation of the glass transition temperature (T_g) of the mixture. Here, the presence of one value for T_g evidences for a thermodynamic compatibility of its components, while the splitting of T_g into two values indicates an incompatibility of polymer components.[1] Information about the polymer mixture T_g is also important in order to establish the temperature region of its applicability and processing. The latter case also indicates the significant role played by the mixture viscosity. Of among the polymer mixtures, poly(methyl metacrylate) mixtures with homo- and copolymers of esters of the metacrylate series turned out to be especially interesting both for scientific studies and practical purposes. This series has a common chain link structure



$$-CH_2-\underset{\displaystyle COOR}{\underset{|}{C}}(CH_3)-$$

where R is the alkyl radical of different lengths. The present paper is devoted to the study of the influence of the copolymer (CP) structures of alkyl metacrylates on T_g, compatibility and viscosity of their mixtures with poly(methyl metacrylate) while systematically varying the CP and mixture compositions.

2. EXPERIMENTAL

The mixtures of poly(methyl metacrylate) (PMMA) with binary statistic CP of methyl metacrylate (MMA) with ethyl (EMA), butyl (BMA) or octyl (OMA) metacrylates as comonomers have been investigated. As an ultimate case, the mixtures of PMMA with poly(ethyl metacrylate)(PEMA), poly(butyl metacrylate)(PBMA) and poly(octyl metacrylate)(POMA) have also been studied. The polymers and CP's were obtained by radical polymerization in bulk of appropriate monomers for 72 h at 313 K in the presence of an initiator—benzoyl peroxide and molecular mass regulator—laurylmercaptane.[2] The molecular masses (M) of the polymers and CP's were measured viscosimetrically.[3] The calculation of M for CP's were made using a hydrodynamic invariant.[3] The polydispersity index M_w/M_n was determined by the method of sediment fractionation. It should be noted that most of the polymers and CP's under investigation had close polymerization degrees, which was achieved by monitoring the content of the initiator and polymerization regulator. The close polymerization degrees rendered it possible to exclude the influence of different polymer and CP chain lengths on their compatibility, T_g and their mixture viscosities. The molecular characteristics of the polymers and CP's as well as their T_g are presented in Table I. Mixtures of PMMA with other polymers and CP's were prepared by mixing given amounts of 20% solutions of the components followed by rapid evaporation of the solvent. The specimens were dried to a constant weight in vacuum at 313–333 K. Methylethylketone was used as the solvent for preparing the PMMA mixtures with PEMA, CP(MMA + EMA), POMA and CP(MMA + OMA), whilst benzene was used as the solvent for

TABLE I

Molecular characteristics and glass-transition temperatures of investigated polymers and copolymers

Nos	Polymer or copolymer	M_w/M_n	Molecular mass × 10^{-5}	Polymerization degree × 10^{-3}	T_g, K
1	PMMA	1.4	1.0	1.0	371
2	PEMA		1.2	1.05	331
3	PBMA	1.8	1.6	1.1	296
4	POMA		1.9	0.98	248
5	CP(75% MMA + 25% EMA)		1.2	1.16	359
6	CP(50% MMA + 50% EMA)		0.82	0.76	351
7	CP(25% MMA + 75% EMA)		0.94	0.85	341
8	CP(85% MMA + 15% BMA)		0.84	0.79	353
9	CP(75% MMA + 25% BMA)		0.91	0.82	347
10	CP(50% MMA + 50% BMA)		1.17	0.96	323
11	CP(25% MMA + 75% BMA)		1.46	1.12	308
12	CP(75% MMA + 25% OMA)		0.80	0.64	338
13	CP(50% MMA + 50% OMA)		0.82	0.55	293
14	CP(25% MMA + 75% OMA)		0.94	0.54	273

preparing the PMMA mixtures with PBMA and CP(MMA + BMA). The cited solvents for the polymers under investigation were "good" ones.[3]

T_g was determined by the thermomechanics method and differential thermal analysis.[4,5] The heating rate was 2° per minute. The T_g values obtained were in appropriate match (±2°) within the errors of the both methods. The mean value of five measurements made was taken for the T_g value. The viscosities of the melts of the investigated systems were determined on capillary viscometers IIRT and AKV-2M.[6] The former used capillaries 25 and 50 mm in length and 2 mm in diameter, the latter employed capillaries 60 and 115 mm in length and 2 mm in diameter. The experimental results were processed according to the generally-accepted technique.[6] The investigations carried out by the two capillary method have shown that the pressure loss due to the input effect for the employed capillaries did not exceed 3–5% and in a number of cases they can be neglected. The melt viscosity of the systems were investigated at 483 K.

3. RESULTS AND DISCUSSION

The dependences of the glass transition temperatures of the PMMA and CP mixtures on the mixture composition are shown in Figures 1–3. In all the cases mentioned, the T_g decreases with decreasing PMMA concentration in the mixture. In the case of CP's (MMA + EMA), all of them up to CP containing 75% EMA form a mixture with PMMA possessing one T_g value at any given concentration; (Figure 1); hence, their compatibility with PMMA over the whole range of the mixture compositions. However, the PMMA + PEMA mixtures possess one T_g value only at PMMA concentrations lesser than 20 or more than 80%. At 20–80% PMMA concentrations, the mixtures possess two T_g values,

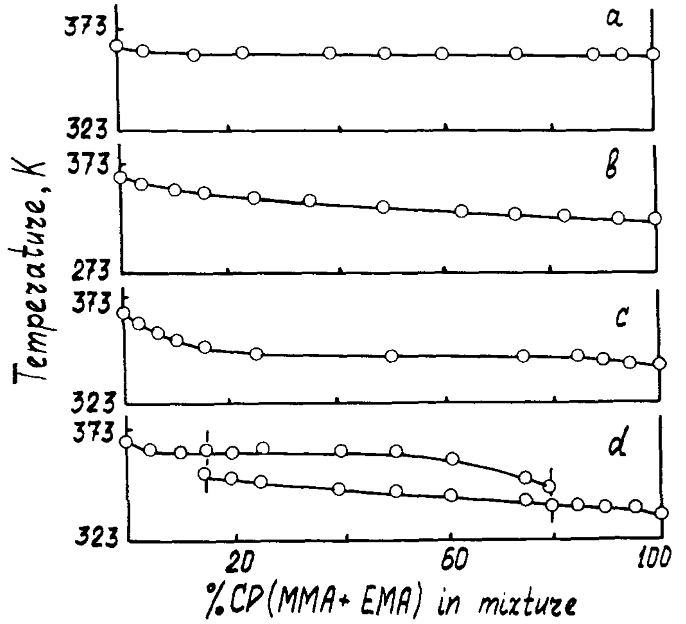


FIGURE 1 Glass transition temperature vs. composition of PMMA–CP(MMA + EMA) mixtures. EMA % in CP: a – 25, b – 50, c – 75, d – 100.

indicating an incompatibility of the both polymers in this region of the compositions. In the case of PMMA with CP containing BMA, only the mixtures of PMMA with CP (85% MMA + 15% BMA) possess one T_g value over the whole range of the mixture compositions (Figure 2). As for the rest of the systems containing CP involving a greater amount of BMA, we observe a splitting of T_g into two values in a broad range of the mixture compositions. An exception of this is only the regions of the limited concentrations containing lesser than 10% CP or 10% PMMA wherein the mixture components appear to be compatible. In the case of PMMA–PBMA mixtures these regions with one T_g value and compatibility of the components narrow down to 5% PBMA or 5% PMMA. For PMMA mixtures with CP's containing OMA and PMMA + POMA mixtures, the narrow regions of compatibility of the mixture components are observed only for the PMMA–CP (75% MMA + 25% OMA) system where the content of CP or PMMA is lesser than 10% (Figure 3). As for the other system, one can observe a splitting of the T_g into two values along the whole range of the mixture compositions.

In Figures 1–3 in the regions of incompatibility of the mixture components the upper curves correspond apparently to the saturated PMMA solution containing a small amount of CP's or the second polymer, whereas the lower curves correspond to the saturated solution of CP or the second polymer containing a small amount of PMMA. This assignment of the phases are based on a natural assumption that the T_g of the PMMA solution containing a small amount of CP or the second polymer is higher than the T_g of the solution of CP or the other

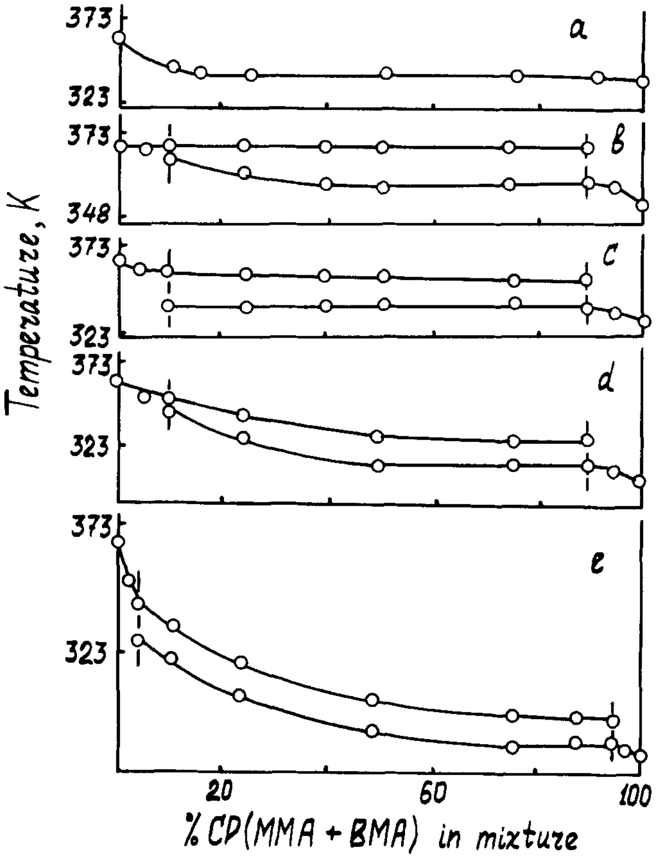


FIGURE 2 Glass transitions temperature vs. composition of PMMA–CP(MMA + BMA) mixtures. BMA % in CP: a – 15, b – 25, c – 50, d – 75, e – 100.

polymer with a small amount of PMMA. The variation of these T_g values with respect to the mixture compositions is worth mentioning. Thus, the T_g value of the PMMA solution containing a small amount of the second polymer or CP component drops with an increase in their content in the mixture, whereas the T_g value CP solutions or the second polymer containing a small amount of PMMA rises with an increase in the PMMA concentration in the mixture. This effect is strengthened by lengthening the radical in the CP or polymer being mixed with PMMA. Such a phenomenon may be due to a number of reasons. One of them is the difference in the thermal coefficients of the mixture phases.[7] A probable reason for the T_g variation in the mixture phases may be the broad molecular-mass distribution of the polymers being mixed. The low-molecular polymer fractions are known to possess a higher solubility in comparison with the high-molecular fractions. Apparently, an increase in the content of the CP mixture or second polymer in mixture should lead to an additional dissolution of their low-molecular fractions in PMMA, lowering T_g of the phase with a preferential content of PMMA. An increase in the PMMA content in the

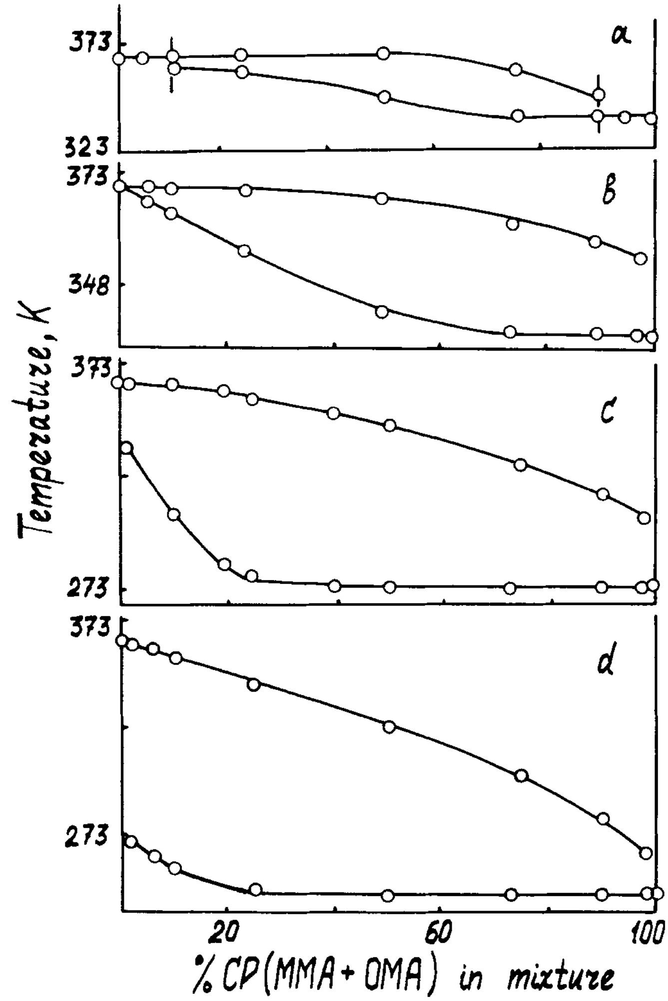


FIGURE 3 Glass transition temperature vs. composition of PMMA-CP(MMA + OMA) mixtures. OMA % in CP: a – 25, b – 50, c – 75, d – 100.

mixture at the expense of additional dissolubility of its low-molecular fraction must raise the T_g phase with a preferential content of CP or second polymer.

On the whole, the data considered indicates that in the case of a small radical length in the comonomers ($R = —CH_2CH_3$), the CP's are compatible with PMMA along the whole or broad range of the mixture concentrations. At the same time, a significant change in the CP composition is possible. However, further lengthening of the radical leads to a dramatic reduction in the copolymer compositions and the region of its concentration in the mixture with PMMA wherein the mixture is in a one-phase state. This conclusion is supported by the data presented in Figure 4, illustrating the dependence of the one-phase mixture concentrations interval, ΔC, on the radical length, R. In this case ΔC stands for a one-phase state region both on the side of the pure PMMA and on the side of the

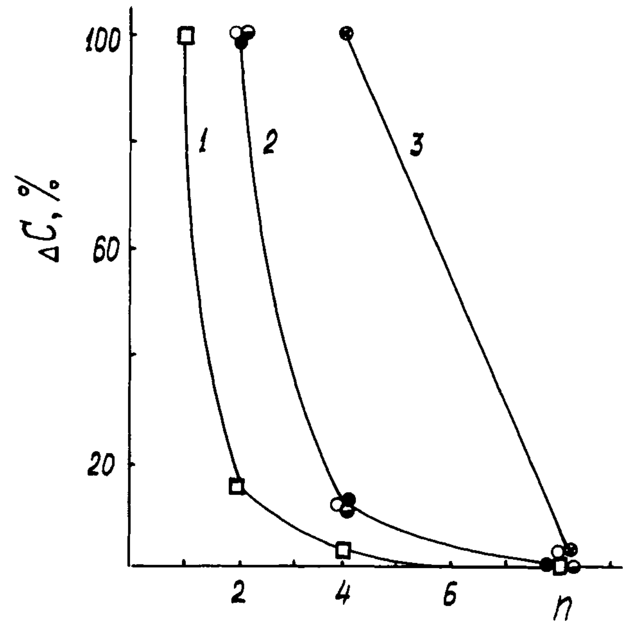


FIGURE 4 Composition ranges ΔC, corresponding to the one phase mixture state vs. n-number of carbon atoms in R of alkyl metacrylate involved in the composition of its copolymer with MMA. Metacrylate % in CP: ⊗ – 15, ● – 25, ○ – 50, ◒ – 75, □ – 100.

pure CP or second polymer. The points indicating mixtures of PMMA with the second polymer and PMMA with the CP's are located on different curves. These curves allow one to arrive at an important conclusion: when CP is added to PMMA, we can introduce into the mixture within the limits of its one-phase state a great deal of links of another polymer than when mixing it directly with PMMA.

The difference in the solubility parameters of the polymers, $\Delta\delta = \delta_1 - \delta_2$, where δ_1 and δ_2 are the solubility parameters of the polymers forming the compositions,[1] can be used as a quantitativeme measure for compatibility evolution. In this case closer values δ_1 and δ_2 presuppose a better polymer compatibility. Figure 5 demonstrates the dependence of the concentration interval, ΔC, on the difference in the solubility parameter of PMMA and the solubility parameter of CP or second polymer in the mixture. These parameters were calculated from the Small's additive scheme from.[8] One can see that the components of the mixtures under consideration prove to be compatible along the whole range of the compositions at $\Delta\delta < 0.4$ $(\mathrm{MJ/m^3})^{0,5}$. At $0.4 < \Delta\delta < 1.2$ $(\mathrm{MJ/m^3})^{0,5}$ the sample polymers appear to be compatible in a fairly narrow concentration range which declines sharply from 10% to 0% with rising $\Delta\delta$. It should be noted that the criterion of compatibility of $\Delta\delta < 0.4$ $(\mathrm{MJ/m^3})^{0,5}$ is close to its value for a number of other polymers.[7]

The viscosities of all the polymer mixtures considered above have been studied in the present work. The change in the viscosity of the polymer mixtures with

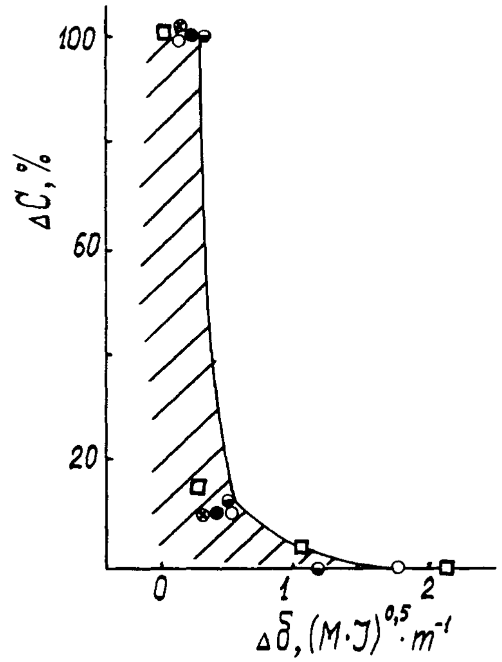


FIGURE 5 Composition ranges ΔC, corresponding to the one-phase mixture state vs. difference in solubility parameters, of PMMA and second mixture component. Same designations as in Figure 4.

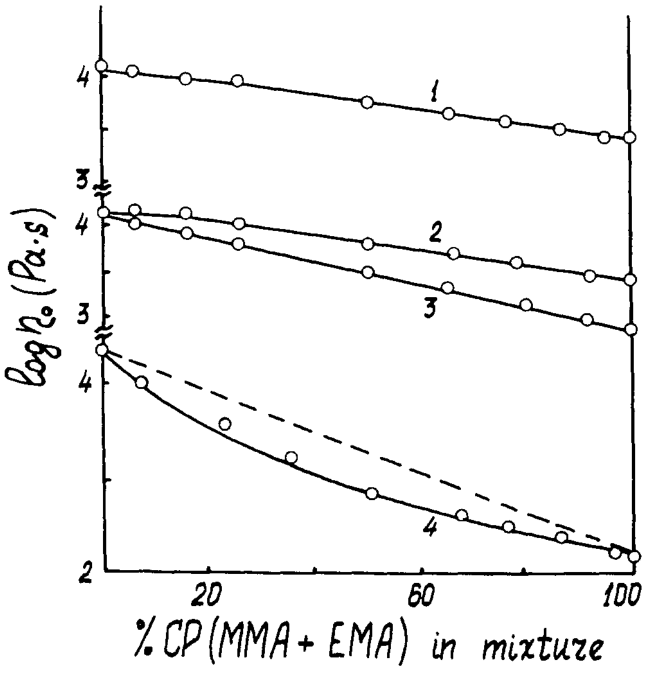


FIGURE 6 Initial Newtonian viscosity vs. PMMA-CP(MMA + EMA) mixtures composition. EMA % in CP: 1 – 25, 2 – 50, 3 – 75, 4 – 100.

their compositions has attracted the attention of many investigators.[7,9,10] Here, one can observe at times a controversary picture depending in particular on the applied mechanical field to the mixture. Therefore our main attention was focussed on the initial Newtonian viscosity corresponding to the flow of the material with a structure which does not change under the action of shear stress or shear rate.

It is seen in Figures 6–8 that when lesser viscous CP's or polymers are added to PMMA, the decrease in the viscosity is general for the majority of the polymer mixtures under investigation. In the case of mixtures whose components are compatible along the whole range of the compositions (mixtures of PMMA with CP's (MMA + EMA) as well as mixtures of PMMA with CP (85% MMA + 15% BMA)) we can observe a linear dependence of viscosity logarithm on the mixture composition. Such an additive dependence is known for a number of compatible low-molecular mass liquids.[7,10] This is conditioned by a similar interaction between all the composition components. The same thing may likely appear valid also in the case of the polymer mixtures under consideration. This is conformed

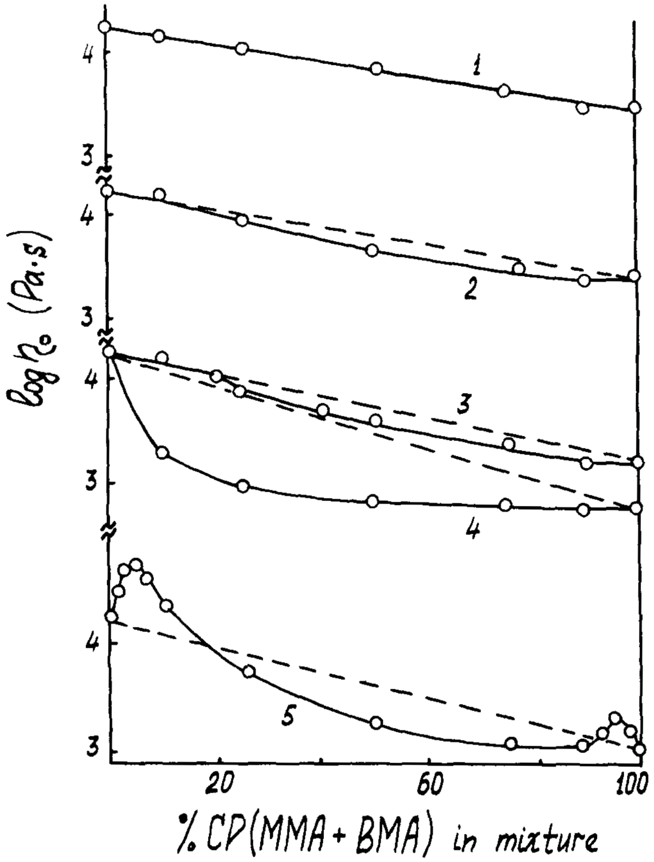


FIGURE 7 Initial Newtonian viscosity vs. PMMA–CP(MMA + BMA) mixtures composition. BMA % in CP: 1 – 15, 2 – 25, 3 – 50, 4 – 75, 5 – 100.

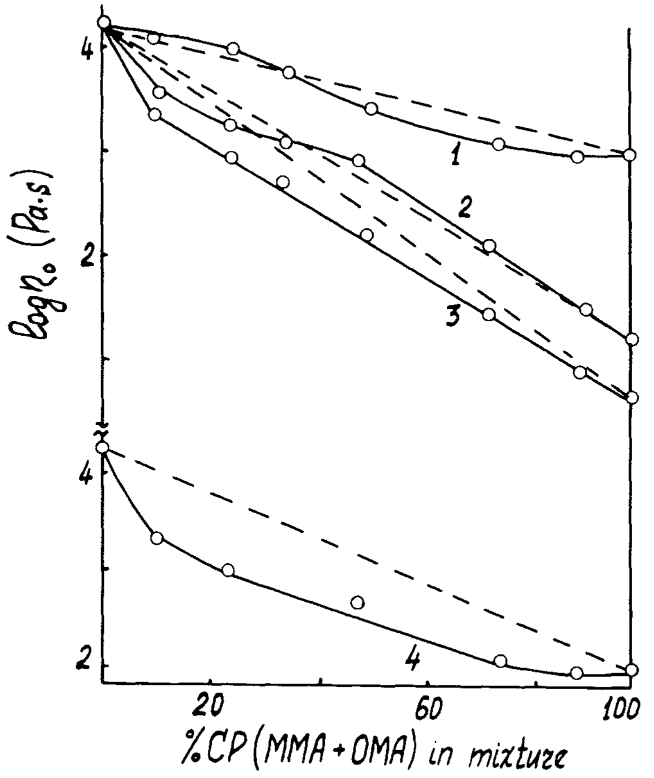


FIGURE 8 Initial Newtonian viscosity vs. PMMA–CP(MMA + OMA) mixtures composition. OMA % in CP: 1 – 25, 2 – 50, 3 – 75, 4 – 100.

by the low values of $\Delta\delta$ in the region of unlimited compatibility of PMMA with its components in mixture. As to the majority of the other mixtures which are incompatible in a broad range of compositions, one observes a negative divergence of the viscosity logarithm from the additive value (Figures 6–8). Such a divergence is likely due to the influence of the interaction of its components on the mixture flow. This is more or less probable in view of the fact that the preparation of the mixtures by stirring their solutions followed by evaporation of the solvent leads to a high dispersity of the components in mixture and to a developed interphase where their interaction takes place. According to data from,[11] it follows that in this case the size of the dispersion of phase particles is of a micron fraction. The incompatibility of the sample mixture components in the absence of a strong specific interaction of the donor-acceptor type, or the interaction forming hydrogen bonds implies a weaker interaction between the phases than an interaction inside of each phase. This apparently leads to a decrease in the viscosity on the whole. The same viewpoint was reported elsewhere.[9] The author presupposes in this case an increase in the free volumes of the phases and believes that this should reduce the mixture viscosity.

Of all the discussed systems, the mixtures of PMMA with CP containing 25 and

50% OMA respectively can be considered as an exception. They demonstrate an *S*-like exchange in the viscosity logarithm with the mixture composition which is rarely found in the literature.[7,10] In those works it is believed that such an exchange in the viscosity is due to the inversions of the phases due to the change in the mixture compositions.[7,10]

Now, in the case of mixtures having a limited components compatibility, one can observe a viscosity maximum in the region of the one-phase mixture state. Such maxima were noticed in the extreme regions during detailed observations (Figure 7, PMMA–PBMA system) the extremal changes in the viscosity are known also for a number of polymer systems in a narrow region of compositions located between the binodal and spinodal of their phase diagram. However, the viscosity passes minimum.[7,9] In our case we observed a different phenomenon. As far back as the 50-ties Semenchenko theoretically showed for low-molecular liquids[12] and in the early 60-ties it was established for concentrated polymer solutions[13] that the viscosity of two-component systems must grow as they approach with a temperature the binodal of the phase diagram due to the occurrence of homophasal density fluctuations. Probably, the very same density fluctuations and the viscosity growth corresponding to them must also occur in the binary polymer systems as they approach with varying compositions the binodal

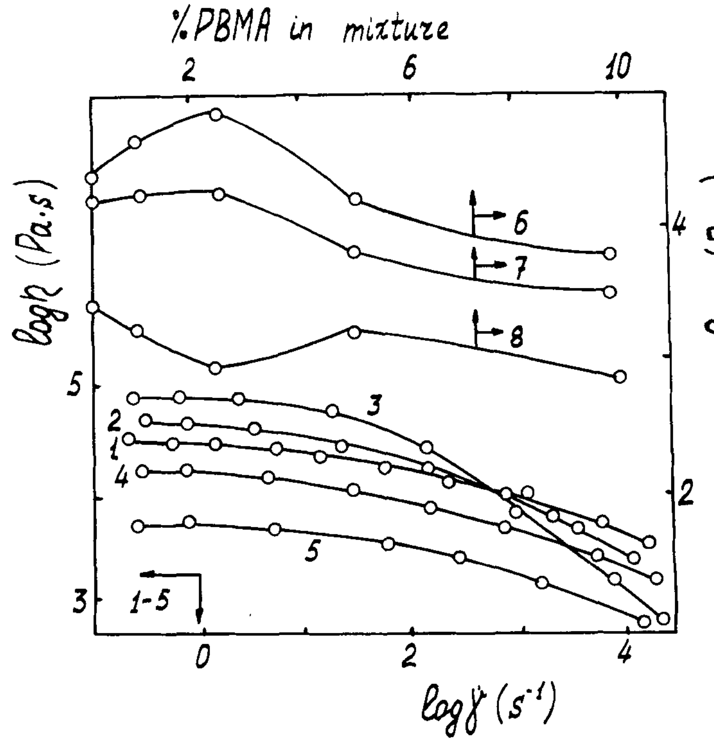


FIGURE 9 Viscosity of PMMA–PBMA mixture vs. shear rate γ(6–8) and PBMA content (1–5). PBMA in mixtures: 1 – 0, 2 – 1, 3 – 2.5, 4 – 5, 5 – 10. γ, sec^{-1}: 6 – 1, 7 – 100, 8 – 1000.

of the phase diagram. Further transition to a two-phase state and completion of the phase decomposition must lead to a drop in the mixture viscosity.[7,9]

Typically, the transition to the Non-Newtonian flow region results in a decrease in the maxima of the PMMA–PBMA viscosity (Figure 9). At high shear rates one observes in this case not a rise but a slight decrease in viscosity. Such a behaviour is apparently due to the dissociation of the density fluctuations with a rise in the shear rate. This leads also to a dependence of the order of mutual position of the curves for the viscosity versus shear rate of one-phase PMMA–PBMA mixtures of varied concentrations on the shear rate value (Figure 9).

CONCLUSION

Thus, the present work demonstrates and predicts the possibility of producing a great number of mixtures of PMMA with copolymers of methyl metacrylate and other alkyl metacrylates which appear to be thermodynamically compatible in different ranges of the mixture composition depending on the nature of its components. In an ultimate case the poly(methyl metacrylate) appears to be compatible with 17% poly(ethyl metacrylate), 5% poly(butyl metacrylate) and practically incompatible with poly(octyl metacrylate). A typical change in the viscous properties of these mixtures depending on the compatibility of their components has been established in this work. The conclusions made in this work are apparently valid also for mixtures of polymer and copolymer metacrylates with molecular masses different from the investigated sample. At any rate, in our experiments on T_g of poly(methyl metacrylate)-poly(butyl metacrylate) mixtures, we have found that a decrease in the molecular mass of the latter from 1.6×10^5 to $6{,}4 \times 10^2$ does not essentially influence the character of the change in the transition temperature with compositions, and, consequently, does not change the range of the regions of compatibility of the mixture components.[14]

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