

Three-Stage Interaction of Dimethyl Phthalate, Dibutyl Phthalate, and Poly(vinyl Acetate) with Poly(methyl Methacrylate)

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Synopsis

The interaction of dimethyl phthalate (DMP), *n*-dibutyl phthalate (DBP), and poly(vinyl acetate) (PVAc) with poly(methyl methacrylate) (PMMA) was studied. Changes in the tensile strength, elastic modulus, and percentage elongation at break of the PMMA-additive films produced were followed using the Instron testing machine. The three additives produced (1) an initial plasticization, with a decrease in tensile strength and modulus and a possible increase in elongation; (2) an antiplasticization, with accompanying increase in tensile strength and modulus and an anomalous increase in elongation; and (3) a final plasticization, with a marked decrease in tensile strength and modulus and a definite increase in elongation of PMMA. The three effects were influenced by the molecular weight of the PMMA. A spacer effect by the interposition of the molecules of the additives between those of PMMA is proposed for the initial plasticization, while for the final plasticization, a lubrication action of the plasticizers on PMMA is suggested. Antiplasticization is explained by the formation of secondary bonds between the antiplasticizer and the PMMA molecules.

INTRODUCTION

Although poly(methyl methacrylate) (PMMA) has been studied extensively and used in several applications, its interaction with small organic molecules and macromolecules has not been given the attention it deserved. It is known, however, that PMMA can be plasticized by several additives, like the conventional plasticizers such as the phthalates, the phosphates, and the sebacates, to mention a few. Ghersa¹ has reported that the interaction of some small molecules with PMMA had produced an effect on the polymer, called antiplasticization, which caused an increase in both the tensile strength and the elastic modulus of the polymer film, with a consequent decrease in its elongation at break. This revelation about antiplasticization was made several years back, and only little additional information concerning PMMA or other polymers, such as those of Jackson and Caldwell² and Sears et al.,³ are now available.

Our work is focused on the interaction of dimethyl phthalate (DMP), *n*-dibutyl phthalate (DBP), and poly(vinyl acetate) (PVAc) with poly(methyl methacrylate) (PMMA). It reports the stages and types of interactions of each of these substances (called additives) with PMMA, and describes the mode of changes in the tensile strength, elastic modulus, and elongation at break of the PMMA samples that accompany the interactions. These are compared for PMMA samples prepared using the same method but of different degrees of polymerization.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) samples were prepared in our laboratory by sulfonated polystyrene free radical-initiated polymerization of methyl methacrylate (MMA) in a dilatometer at 86°C, as described by Olayemi and Adeoye.⁴ Polymerization was carried out for 5 hr using different volumes of water, a constant volume of MMA, and 0.2 g resin initiator (Na⁺ form) to obtain PMMA samples of different degrees of polymerization (\bar{P}_n), between 8.5×10^3 and 11.5×10^3 , as determined by viscosity measurement and Welch's equation.⁵ The poly(vinyl acetate) sample used was also produced in our laboratory by a 6-h emulsion polymerization of vinyl acetate (VAc) at 60°C. The solid polymer was separated from its emulsion and purified by the method described by Obande.⁶ Its viscosity-average molecular weight (\bar{M}_v), 8.63×10^5 , was determined from the Mark-Houwink-Sakurada equation, with $K = 66 \times 10^{-3} \text{ cm}^3/\text{g}$ and $a = 0.53$ in benzene⁷ at 27°C. Benzene, chloroform, methanol, ethanol, dimethyl phthalate, and *n*-dibutyl phthalate were from the British Drug Houses Ltd and were of the highest purity available. They were used with no further purification.

Mixing of PMMA and the Additives to Produce Films

A suitable volume of stock PMMA solution in chloroform was measured into a small glass bottle equipped with a tight-fitting lid and treated with the required quantity of DMP, DBP, or PVAc in chloroform. Sufficient chloroform was added to give approximately 15 cm³ of the mixture in the bottle. The bottle was covered tightly and shaken for 48 h in a water bath, and maintained at 26°C, after which the contents of the bottle were poured on mercury contained in a suitable basin and the solvent allowed to evaporate over a period of 36 h. The thin PMMA film left on the mercury surface was recovered carefully and kept at 26°C and 65% relative humidity (RH) for a period of 60 h prior to testing. A transparent film of PMMA additive of uniform thickness of approximately 0.1 mm was obtained. Various quantities of each additive were used against various quantities of PMMA (for PVAc) in order to obtain different weight percentages of the additives in the system.

Testing of Polymer Films

The tensile strength, elastic modulus, and percentage elongation at break of each film were determined on an Instron testing machine, model 1026, using a strain rate of 50 mm/min. Measurements were carried out at 26°C and 65% RH on several strips of uniform dimensions of 2.5 and 1 cm gauge length and width, respectively, cut out from the PMMA-additive films.

RESULTS AND DISCUSSION

The results of this investigation indicate that interaction of DMP, DBP, and PVAc with PMMA is in three stages which depend on the weight percent of the additive in the PMMA-additive system. On the basis of the effects produced by the individual additives on PMMA, the three-stage interactions are classified

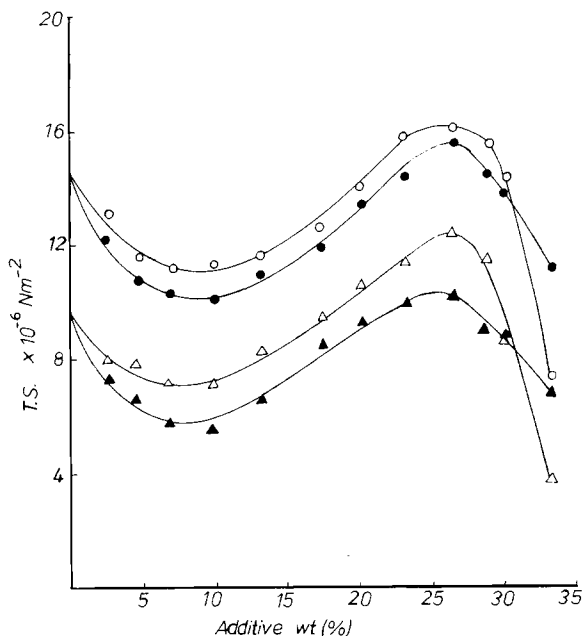


Fig. 1. Effect of additives on tensile strength (T.S.) for PMMA of different \bar{P}_n : (●) and (▲) for DMP; (○) and (△) for DBP; circles for $\bar{P}_n = 11.1 \times 10^3$, and triangle for $\bar{P}_n = 8.8 \times 10^3$.

as (1) initial plasticization, (2) antiplasticization, and (3) final plasticization of PMMA. Figure 1 indicates how the tensile strength of PMMA varies with the concentration of DMP and DBP. A similar behavior was observed for elastic modulus of PMMA on treatment with DMP and DBP. The three stages of interaction are conspicuous. Initial plasticization exhibits a maximum at about 7%, while antiplasticization is maximum at 26% weight of DMP or DBP. Initial plasticization decreases as the molecular size of the additive increases.

During the initial plasticization, tensile strength and elastic modulus of PMMA decrease while elongation might increase. Following this is antiplasticization, producing an increase in tensile strength and elastic modulus with a slight reduction in elongation of the polymer, especially just prior to the commencement of antiplasticization. Final plasticization of PMMA occurs beyond a critical concentration (C_s) of the additives, shown in Table I. In this region, tensile strength and elastic modulus of PMMA decrease while elongation increases on treatment of the polymer with DMP or DBP.

TABLE I
Mean Values of Some Parameters Obtained from the Interaction of DMP, DBP, and PVAc with PMMA

Additive	Weight additive, %		Critical plasticizer concentration (C_s), wt %	
	Peak of Initial plasticization	Peak of Antiplasticization	Tensile strength study	Modulus study
DMP	7	26	29	30
DBP	7	26	30	31
PVAc	4	40	87	58

For a given sample of PMMA, DBP is less efficient in the initial plasticization of PMMA than DMP, but more so in the antiplasticization and final plasticization that follow. The effectiveness of DMP and DBP in producing changes in the tensile strength of PMMA has been compared graphically in Fig. 2 for polymer samples of different degrees of polymerization, \bar{P}_n . An inverse and linear relationship between specific tensile strength, defined as change in tensile strength of PMMA due to the additive compared to the tensile strength of the pure PMMA, and \bar{P}_n is observed for the antiplasticization of PMMA for the range of \bar{P}_n investigated. For initial plasticization of PMMA, specific tensile strength varies directly with \bar{P}_n . The results observed in respect of specific modulus of PMMA are omitted but are similar to those of specific tensile strength, for both antiplasticization and initial plasticization of the polymer by DMP and DBP.

Figure 3 indicates that an insignificant decrease in elongation occurs immediately at the end of initial plasticization of PMMA by DMP or DBP and is immediately followed by a significant but somewhat unexpected increase in elongation in the region of effective antiplasticization.

Figures 4 and 5 represent the results obtained for the blends of PMMA and PVAc. The results for only two PMMA samples with different \bar{P}_n are presented for clarity. The initial plasticization of PMMA by PVAc is small, with insignificant changes in the three mechanical properties studied. The antiplasticization region is wide and exhibits a peak at 40% weight PVAc. It increases with the \bar{P}_n of PMMA, to which it bears a linear but inverse relationship in terms of specific tensile strength and specific modulus of the polymer (Fig. 6). Elongation of PMMA increases with weight of PVAc over the entire range of the latter, as shown in Fig. 7.

The initial plasticization of PMMA by DMP, DBP, or PVAc is assumed to be produced by the interpolation of the additive molecules between those of PMMA.

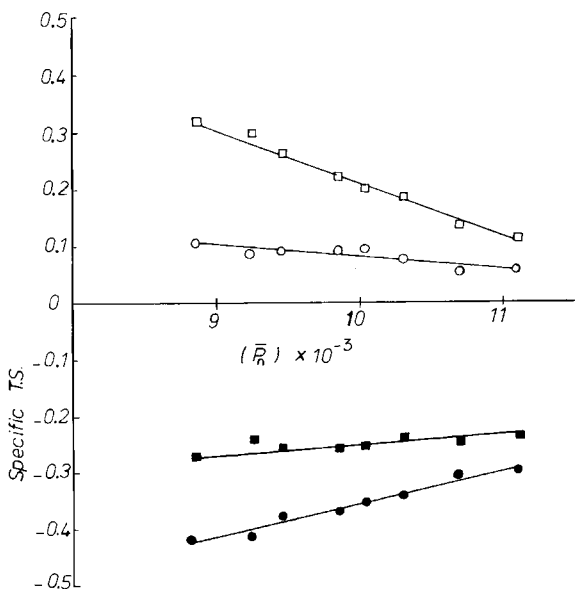


Fig. 2. Variation of specific tensile strength of PMMA with \bar{P}_n at the peaks of initial plasticization and antiplasticization with (●) and (○) respectively for DMP; (■) and (□) respectively for DBP.

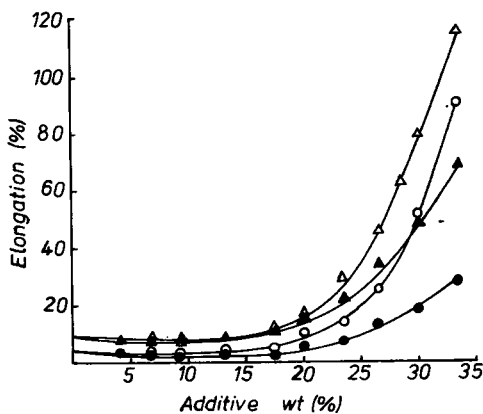


Fig. 3. Effect of additives on the percentage elongation at break of PMMA of different \bar{P}_n : (●) and (▲) for DMP; (○) and (△) for DBP; circles for $\bar{P}_n = 11.1 \times 10^3$ and triangles for $\bar{P}_n = 8.8 \times 10^3$.

For a porous polymer like PMMA, this type of interpolation of additive molecules between those of PMMA is easy. The interaction between the additive molecules and those of PMMA is nonspecific, and its equilibrium is dynamic at the initial plasticization stage, as fewer interacting sites are available from the additives than are required by the polymer.

At higher concentrations of additive, polymer-additive interaction increases, with an equilibrium being established. Increase in specific interaction between additive and PMMA continues until its effect is maximum at the peak of antiplasticization. The system consequently becomes highly ordered as molecular motions are restricted due to formation of secondary bonds like hydrogen bonds and van der Waals interactions between the polymer and additive molecules, as suggested by Ghersa.¹ Crosslinking of the PMMA molecules by additive molecules is proposed, and its effectiveness would depend on the molecular size

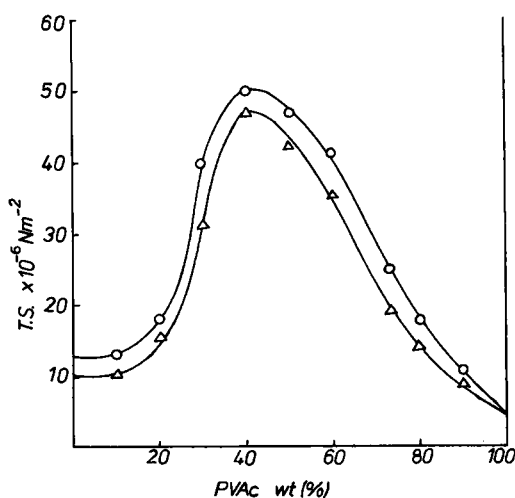


Fig. 4. Effect of PVAc on the tensile strength (T.S.) for PMMA: (○) $\bar{P}_n = 10.3 \times 10^3$; (△) $\bar{P}_n = 9.4 \times 10^3$.

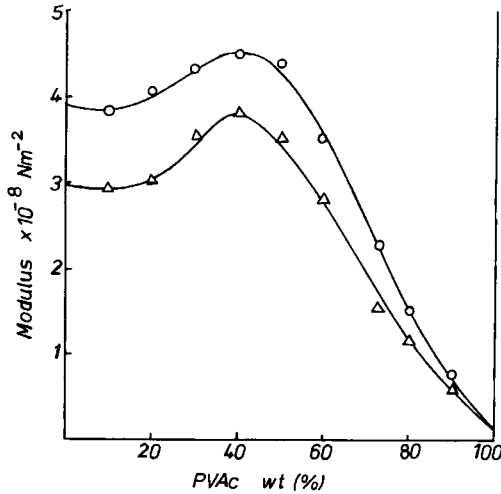


Fig. 5. Effect of PVAc on the elastic modulus of PMMA: (O) $\bar{P}_n = 10.3 \times 10^3$; (Δ) $\bar{P}_n = 9.4 \times 10^3$.

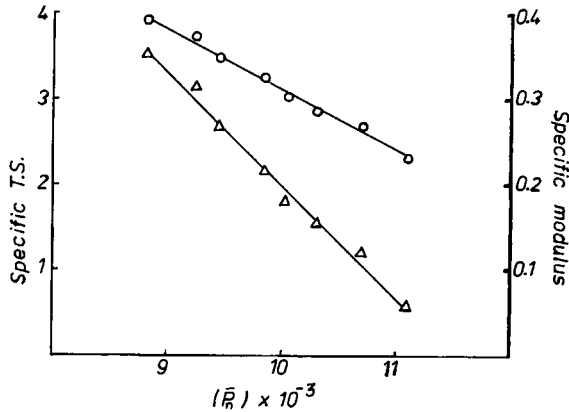
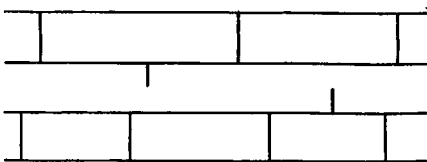
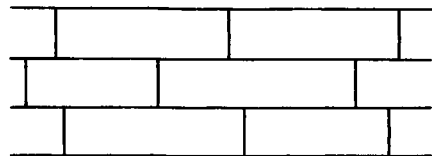


Fig. 6. Variation of specific tensile strength (O) and specific modulus (Δ) of PMMA with \bar{P}_n at the peak of the antiplasticization with PVAc.

of the additive, the bigger molecules being more effective. Also, at the antiplasticization stage, the polymer-additive system would have a smaller specific volume, an observation made earlier in the study of antiplasticization of poly(vinyl chloride).⁸ The peak of antiplasticization actually reveals an increase in elongation. In order to explain this anomalous increase in elongation that accompanies antiplasticization, a form of simple crosslinking of the polymer molecules of additoids is proposed, which avoids formation of a continuous and extensive network of crosslinking:



Simple crosslinking of horizontal PMMA molecules through the vertical molecules of additive.



Continuous and extensive network of crosslinking.

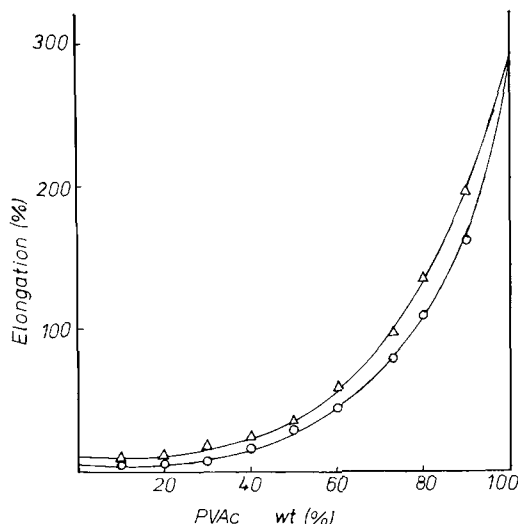


Fig. 7. Effect of PVAc on the percentage elongation at break of PMMA of different \bar{P}_n . Circles for $\bar{P}_n = 10.3 \times 10^3$; triangles for $\bar{P}_n = 9.4 \times 10^3$.

This is possible with PMMA with a rigid backbone and predominantly syndiotactic structure. The formation of dimers of PMMA molecules which still maintain some interdimer interactions would cause an increase in tensile strength and modulus and yet permit some movements within the system.

At the final plasticization stage, the additives serve as lubricants, as earlier suggested.⁹ Secondary bonds between polymer and additive molecules might still be present, though their life time could be so small as to make their formation a dynamic process. This is due to the large volume of the plasticizer present which has the effect of reducing even the attractive forces between the polymer chains. It is only beyond the critical plasticizer concentration (C_s), given in Table I, that Flory¹⁰ and Boyer¹¹ equations are expected to apply, showing an inverse and linear relationship between tensile strength and weight percent plasticizer. The large increase in elongation and significant decreases in tensile strength and modulus of PMMA that follow after the critical plasticizer concentration are expected in the region of the final plasticization by DMP or DBP. By our previous explanation in terms of molecular size, it is not surprising that DBP is more efficient than DMP in producing an increase in elongation of PMMA in the region of final plasticization. Lawrence et al.¹² have reported similar observations for some resins.

The small changes in tensile strength, modulus, and elongation of PMMA at the initial plasticization stage for the PMMA-PVAc system are expected for an additive (PVAc) of a macromolecular size. For the antiplasticization stage, PVAc can be regarded as sandwiched between the molecules of PMMA, thus causing an increase in the density of the latter which is also more compressible than the former. Consequently, the tensile strength and modulus of PMMA increase to a maximum, then decrease to their value for the pure PVAc sample. The values of C_s observed for PVAc, reported in Table I, are different. This is probably due to the usually larger difference^{13,14} between the moduli of PMMA and PVAc compared to the difference in the tensile strengths of the two separate

polymers, especially if a well-defined peak of antiplasticization is to occur at 40% PVAc, as in Figs. 4 and 5. Elastic modulus of PMMA therefore changes more rapidly than the tensile strength does on increasing the weight percent of PVAc in the blend.

CONCLUSIONS

Our results indicate that DMP, DBP, and PVAc interact with PMMA when mixed in chloroform solution, and the films produced on mercury surface are clear and colorless. There is (1) initial plasticization of PMMA involving a decrease in the tensile strength and elastic modulus, with no significant change in elongation; (2) an antiplasticization immediately following the initial plasticization, and reflecting an increase in the tensile strength and elastic modulus, and an anomalous increase in elongation; and (3) a final plasticization of PMMA, leading to a decrease in the tensile strength and elastic modulus and a significant increase in elongation.

The initial plasticization of PMMA is pronounced with DMP and DBP and goes through a maximum value at about 7% weight of the additive, with DMP having the greater effect. With PVAc, the effect is very small. Antiplasticization of PMMA is largest with PVAc and smallest with DMP, among the three additives. It exhibits a maximum at 40% with PVAc and 26% with DMP and DBP.

Poly(vinyl acetate) is far more efficient than DMP or DBP in increasing the tensile strength, elastic modulus, and elongation at break of PMMA at the concentration corresponding to the peak of antiplasticization. However, it is the least efficient in increasing the elongation of PMMA at the final stage of plasticization where DMP or DBP are excellent.

The extent of each of the three stages of interaction of DMP, DBP, and PVAc with PMMA is influenced by the molecular weight of PMMA.

Although the tests for permanence and heat resistance of these additives in the PMMA—additive systems were not conducted in our study, it is held that our results would serve as a good start for our ongoing search. We also believe that blending of PMMA with PVAc gives a product with properties that could be close to those of the so much desired, but yet difficult to produce, copolymer of MMA and VAc. It is also hoped that with our results, the antiplasticization of PMMA by small molecules and macromolecules would now be better understood and its technological consequences considered.

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