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Mechanical Properties of Diallyl Phthalate Resins Co-Cured Microheterogeneously with Vinyl Monomers Having Long-Chain Alkyl Groups

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Summary

Diallyl phthalate(DAP) was co-cured with vinyl monomers having long-chain alkyl groups, including vinyl laurate(VL), dioctyl fumarate(DOF), lauryl methacrylate(LMA), and stearyl methacrylate(SMA) with the intention of the improvement in mechanical properties of commercially important DAP resins. Thus the elongation and fracture energy increased with an increase in the mole fraction of comonomers and their extents were enlarged in the order VL $<$ DOF $<$ LMA $<$ SMA, although a reverse tendency was observed for the tensile strength; in particular, LMA and SMA as comonomers showed a remarkable effect. These results are discussed in detail by considering the copolymerizability of DAP with comonomers and, moreover, the formation of microgel in microheterogeneous copolymerization systems.

Introduction

In our previous article(1) diallyl phthalate(DAP) as a commercially important monomer was co-cured with glycol bis(allyl phthalate)s with the intention of the improvement in their mechanical properties; the introduction effect of flexible crosslinked units into DAP resins was reflected in the improved flexibility, particularly the effect of polyethylene glycol bis (allyl phthalate)(PEGBAP) having a long-chain glycol unit being remarkable. This was interpreted in connection with the fact that the microgel formation occurs rapidly in the conversion range of 25-50%, i.e., beyond the gel-point conversion and, then, the microgels agglomerate to the macrogel(2). That is, the polyethylene glycol unit in PEGBAP can't be compatible with DAP polymer chain and, therefore, most of the PEGBAP units incorporated into the DAP polymer chain may come to exist on the surface of the microgel, effectively playing an important role for crosslinking of microgels to form the macrogel; this might result in the formation of flexible units between rigid microgels.

The above discussion prompted us to explore the co-curing of DAP with vinyl monomers having long-chain alkyl groups because the polymer chains having less polar, long-chain alkyl groups which are not compatible with DAP polymer chain can exist predominantly on the surface of the microgel, resulting in the formation of flexible crosslinked units. Here vinyl laurate(VL), dioctyl fumarate(DOF), lauryl methacrylate(LMA), and stearyl methacrylate(SMA) were chosen as comonomers having long-chain alkyl groups. In this connection, Usmani and Salyer (3) have, noticeably, reported during the progress of this investigation that the flexibilized DAP resins for encapsulating electronic display devices could be obtained from the copolymerization of DAP with LMA and SMA, although the reason for the improved flexibility was not discussed from a mechanistic standpoint.

Experimental

DAP as a monomer, obtained commercially, was subjected to distillation in vacuo under nitrogen.

VL, DOF, LMA, SMA, and butyl methacrylate(BMA) as comonomers, and benzoyl peroxide and dicumyl peroxide as curing agents were used as commercially available extra pure reagents.

Curing procedure and measurements of mechanical properties were carried out similarly as described previously(1), except that in the case of the co-curing of DAP with BMA, the first stage heat-treatment was conducted at 60°C for 10 h in place of the heat-treatment at 80°C for 5 h because of the low boiling point of BMA.

Results and Discussion

Figure 1 shows the dependences of tensile strength of the co-cured DAP resins on monomer composition in the co-curing of

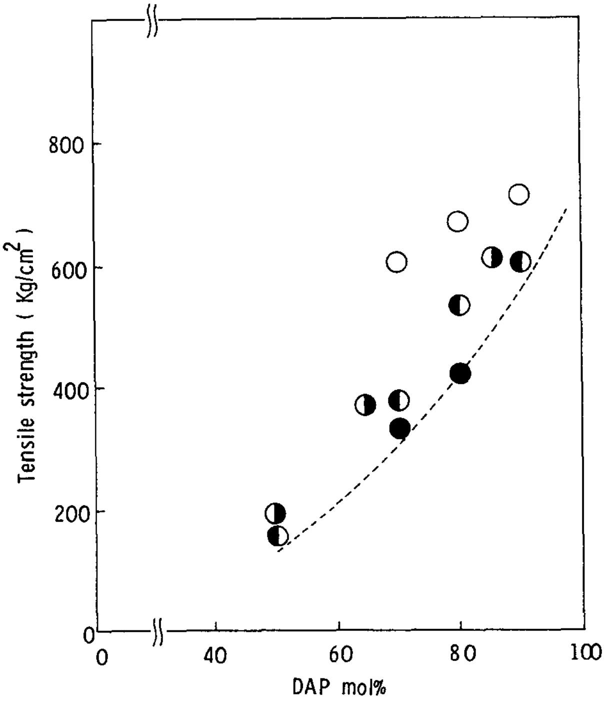

Figure 1.

Dependences of tensile strength on monomer composition for the DAP resins co-cured with (○) VL, (◑) DOF, (◐) LMA, (●) SMA, and (----) PEGBAP.

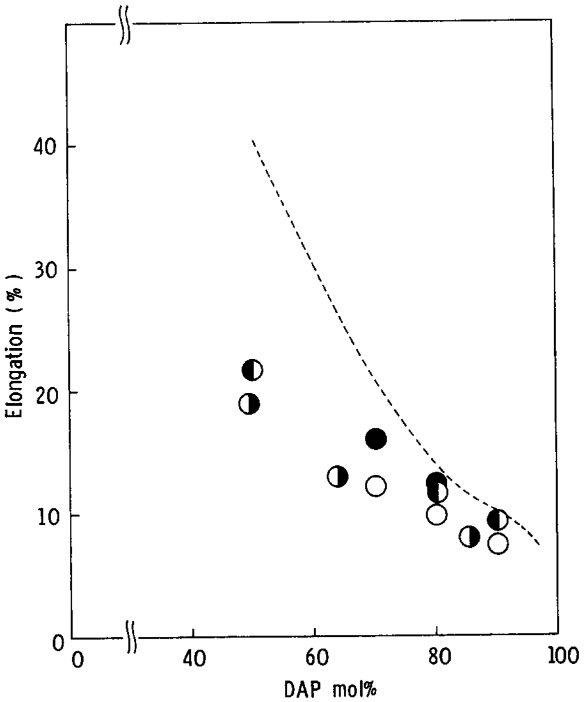

Figure 2.

Dependences of elongation on monomer composition for the DAP resins co-cured with (○) VL, (◑) DOF, (◐) LMA, (●) SMA, and (----) PEGBAP.

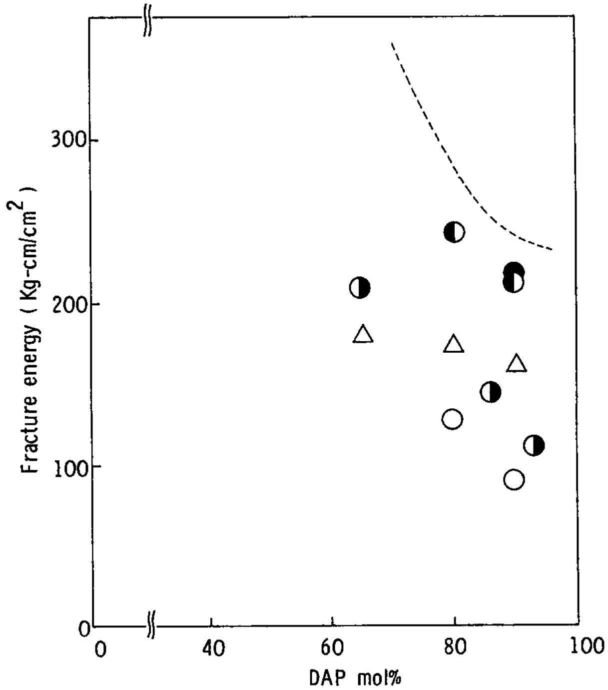

Figure 3.

Dependences of fracture energy on monomer composition for the DAP resins co-cured with (○) VL, (◑) DOF, (◐) LMA, (●) SMA, (△) BMA, and (----) PEGBAP.

DAP with VL, DOF, LMA, and SMA; the tensile strength decreased with an increase in the mole fraction of comonomers and its dependency tended to be remarkable in the order VL < DOF < LMA < SMA. Particularly, the addition effects of LMA and SMA were quite great, being comparable to the result of PEGBAP as the dotted line in Figure 1.

Figures 2 and 3 show the relationships between elongation or fracture energy and monomer composition; as a reverse tendency to the case of the tensile strength shown in Figure 1, both elongation and fracture energy increased with increasing the mole fraction of comonomers and their extents were enlarged in the order VL < DOF < LMA < SMA.

Thus the introduction effect of long-chain alkyl groups into the DAP resins was reflected in the improved flexibility. In particular, LMA and SMA as comonomers showed a remarkable effect; for example, the DAP resin co-cured with 10 mol% of LMA had the tensile strength of 600 Kg/cm^2, the elongation of 9.0%, and the fracture energy of 215 Kg/cm^2, although the DAP resin obtained by homopolymerization was quite brittle and, therefore, could not even be subjected to the measurement of mechanical properties. In order to interpret these results the copolymerizability of DAP with the comonomers employed should be first discussed, in addition to the consideration of the comonomers in the copolymerization process to form the microgel and, moreover, macrogel. In this connection, we have investigated in detail the copolymerization of DAP(M_1) with vinyl monomers(M_2) (4-6), the copolymerization parameters for which were estimated as follows: M_2 , r_1 , r_2 ; vinyl acetate(VAc), 0.82, 0.88 (at 80°C); DOF, 0.02, 0.96 (at 60°C); methyl methacrylate(MMA), 0.057, 35.0 (at 80°C). Here the r_1 and r_2 values correspond to those for one allyl group of DAP, the values which were calculated from eq.(1) derived by assuming the nonoccurrence of the intramolecular cyclization reaction of DAP(6).

$$\frac{d[M_1]}{d[M_2]} = \frac{2[M_1]}{[M_2]} \cdot \frac{2r_1[M_1] + [M_2]}{2[M_1] + r_2[M_2]} \qquad (1)$$

By considering that the r_1 and r_2 values for VAc or MMA may approximately correspond to those for VL or LMA and SMA, respectively, we can now calculate the composition of the copolymer formed at any instance, the composition which changes with the progress of polymerization, according to the method of Skeist (7); Figure 4 shows the variation of the instantaneous copolymer composition with conversion for a starting monomer composition of 20 mol% of M_2 for the copolymerization of DAP(M_1) with VL, DOF, and LMA(or SMA)(M_2) as an example; in the case of LMA the copolymer composition was rapidly changed from the initial value of 78.7 mol% of M_2 to 2.3 mol% at 50% conversion, whereas for the DAP-VL copolymerization the slow change was observed as the opposite tendency accompanied by the increase in the mole fraction of M_2 with conversion.

Thus, on the DAP-LMA copolymerization process leading to the microgel formation the initially obtained copolymers of high LMA contents can't be compatible with DAP-enriched polymer chains which increased rapidly with the progress of polymerization, and, therefore, they may exist predominantly at the space

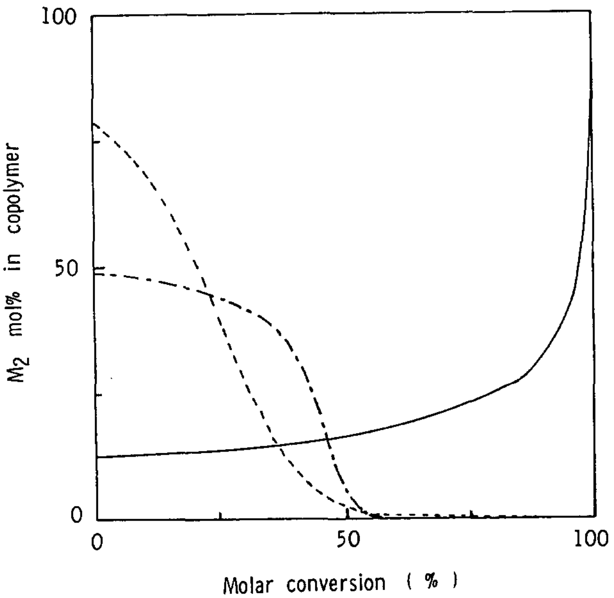

Figure 4. Variation of the instantaneous copolymer compositions with conversion for a starting monomer composition of 20 mol% of M_2 for the copolymerization of DAP(M_1) with (——) VL, (—·—) DOF, and (----) LMA(M_2).

among microgels, acting as flexible crosslinkers of microgels to form the macrogel. On the other hand, in the DAP-VL copolymerization system the copolymer compositions don't change considerably with conversion as shown in Figure 4; the long-chain alkyl groups incorporated uniformly into the DAP chain may come to exist favorably on the surface of the microgels, forming a local, non-polar environment where the concentration of unreacted VL monomer may be increased leading to a microheterogeneous polymerization, although the extent of heterogeneity should be low compared with DAP-LMA copolymerization.

As an extension of the above discussion, the addition effect of LMA is expected to be lessened by replacing LMA by BMA because the polarity of BMA is close to DAP and, therefore, the extent of microheterogeneity will be reduced: In Figure 3 is plotted the fracture energy of DAP-BMA co-cured resins against monomer composition; the fracture energy decreased and its monomer composition dependency was small compared with DAP-LMA co-cured resins as expected.

Elucidation of the details of the microheterogeneous copolymerization behavior of DAP with vinyl monomers having long-chain alkyl groups is now being investigated in connection with the microgel and, moreover, macrogel formation.

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