

Polyester Molding Compounds: Partial Systems and Related Particulate Composites

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Synopsis

Several binary or ternary systems, consisting of an unsaturated polyester resin and one or two additives which are currently considered in formulating polyester molding compounds (such as BMC and SMC) were studied in relation to some of their relevant properties as a function of their composition. The additives were: MgO as a thickening agent; a thermoplastic polymer (PS or PVAc); and a fine CaCO₃ particulate filler. Measured quantities were, depending on the system physical state (fluid or crosslinked): viscosity, linear shrinkage, flexural modulus and strength, and fracture toughness and energy, besides SEM morphological characterization. Quantitative relations could in several instances be expressed; in particular, the relation between strength and filler volume fraction was found to follow the linear equation of the simplest area reduction "random model."

INTRODUCTION

Thermosetting polymers are being used increasingly as matrix materials in reinforced plastics and composites. Particularly intensive is the use of unsaturated polyesters in complex compounds, of a rubbery consistency, prevalently containing mineral fillers and glass fibers, which are then transformed into end articles by hot molding crosslinking of the resin.

A notable case is that of bulk molding compounds (BMC) and sheet molding compounds (SMC), the latter suitable for end articles with a large surface and a small thickness (a few mm), also able to replace metals economically. An example of SMC composition may be the following: 30% weight unsaturated polyester/styrene + thermoplastic polymer; 40% CaCO₃; 25% glass fiber and 5% other additives.¹

The aim of this work is to improve the present knowledge of the relationship between composition and mechanical, or rheological, properties of some binary or ternary systems that become the matrix of fiber-reinforced materials.

EXPERIMENTAL

Materials

The starting material of the present study was a commercial unsaturated polyester resin (Neoxil 235, SAVID S.p.A., Como, Italy) with the following molar composition: 1 mol of phthalic anhydride, 1 mol of maleic anhydride, 2.1 mol of propylene glycol, and a few % of trimethylol propane. The

commercial polyester resin contains 33% styrene. In order to reduce the polyester/styrene viscosity, styrene was added to the resin up to 50% weight. An experimental polyester resin (which will be referred to as "modified resin") with a composition slightly modified in order to give some chemical interaction with CaCO_3 was also used. The thickening agent was a suspension of magnesium oxide in styrene. Thermoplastic additives included polystyrene (PS) (BASF 158 K) and polyvinylacetate (PVAc) (Union Carbide LP 40). Calcium carbonate powder (particle size 3 μm , MILLICARB OMYA 2030) was also added to the uncatalyzed polyester.

The curing system comprised 1% by weight of methyl-ethyl ketone peroxide (Butanox M-50, AKZO Chemie) and 0.5% of a 6% cobalt naphthenate solution in styrene.

The resin-initiator-accelerator mixture was cast between glass plates separated by 6 mm thick rubber strips. The curing period included 2-3 days at 22°C followed by postcuring at 80°C for 8 h.

Methods

Specimens for mechanical testing were cut from the molded plates by a disk saw and then polished by emery cloth.

Flexural modulus E and strength σ were measured on $126 \times 12.6 \times 6$ mm specimens by an Instron Dynamometer 1121-10 KN, with a three-point bending of unnotched specimens (span: 100 mm, crosshead speed: 1 mm/min). The fracture toughness K_{Ic} , and consequently the fracture energy G_{Ic} , was measured according to ASTM E-399, on $63 \times 12.6 \times 6$ mm sharply notched specimens (span: 50 mm, crosshead speed: 1 mm/min). Every experimental value is given as an average from 10 to 16 specimens, with the indicated standard deviation.

Viscosity was measured at 25°C by a Brookfield RVT viscometer.

RESULTS AND DISCUSSION

Resin-MgO system

It is known that, by addition of relatively small amounts of an oxide or hydroxide of metals such as Mg or Ca (thickening agent), an appropriate polyester resin undergoes a thickening process, by which the system viscosity increases up to a plateau value in a time of a few or several hours.

The thickening process has been the object of several studies.²⁻¹⁰ It is due to the interaction of acidic or alcoholic end groups of the polyester with the thickening agent, that, depending on the conditions, leads to the formation of neutral or basic salts, as well as of metal complexes with hydroxyl or carbonyl oxygens. A kinetic model has been also formulated,^{7,8} which, however, predicts the observed features only qualitatively.

The thickening actually proceeds through three stages: (a) induction period; (b) substantial viscosity increase; (c) achievement of the plateau value.

In Figure 1 are reported our systematic results of viscosity measurements, as a function of time, of the polyester resin with different additions of MgO. The system viscosity is expressed as "relative" viscosity, i.e., as the ratio between the actual viscosity η and the initial viscosity η_0 .

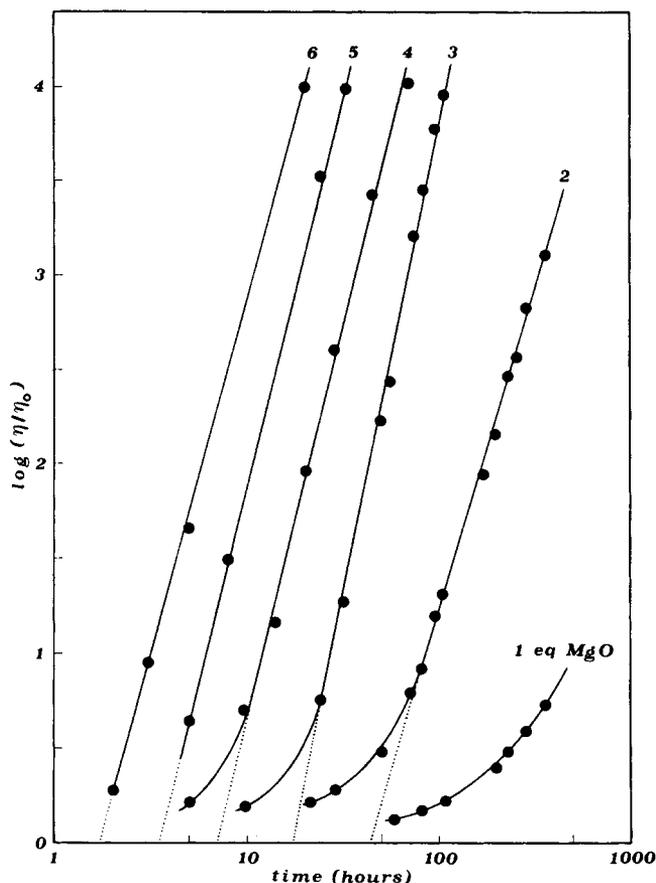


Fig. 1. Relative viscosity (referred to the initial viscosity η_0) vs. time, showing the thickening of the polyester resin for various addition of MgO (expressed as equivalents with respect to the total free acid groups of the resin). Straight lines according to eq. (1).

The measurements were performed up to $7 \times 10^4 P$, and therefore below the plateau value (around $1 \times 10^6 P^{-1}$), but the first two stages of the process are clearly singled out. In particular, the main stage of the substantial viscosity increase follows, in the bilogarithmic plot, a straight line, which can be expressed by the equation

$$(\eta/\eta_0) = (t/t_i)^a \quad (1)$$

where t_i may be defined as an induction time, i.e., the time value extrapolated at $\eta/\eta_0 = 1$. This depends on the amount q of MgO added to the resin, and can in turn be expressed by the equation

$$t_i = b/q^c \quad (2)$$

In our conditions we found $a \cong 4$ and $c \cong 3$, whereas b had a constant value, likely dependent at least on the reaction ability of the specific MgO particles used and on the water content of the system.

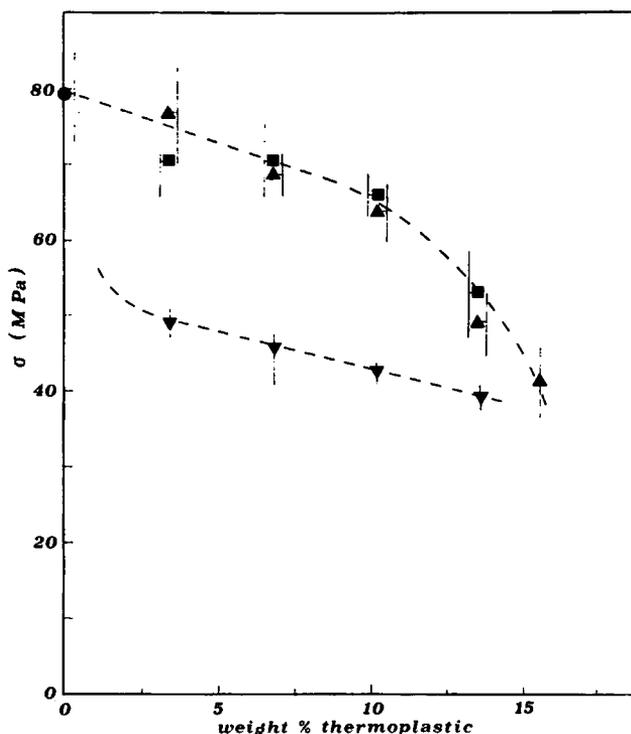


Fig. 2. Effect of addition of PS, (▲) fine dispersion, and (▼) coarse dispersion, and PVAc (■) on the flexural strength of the cured resin-thermoplastic system.

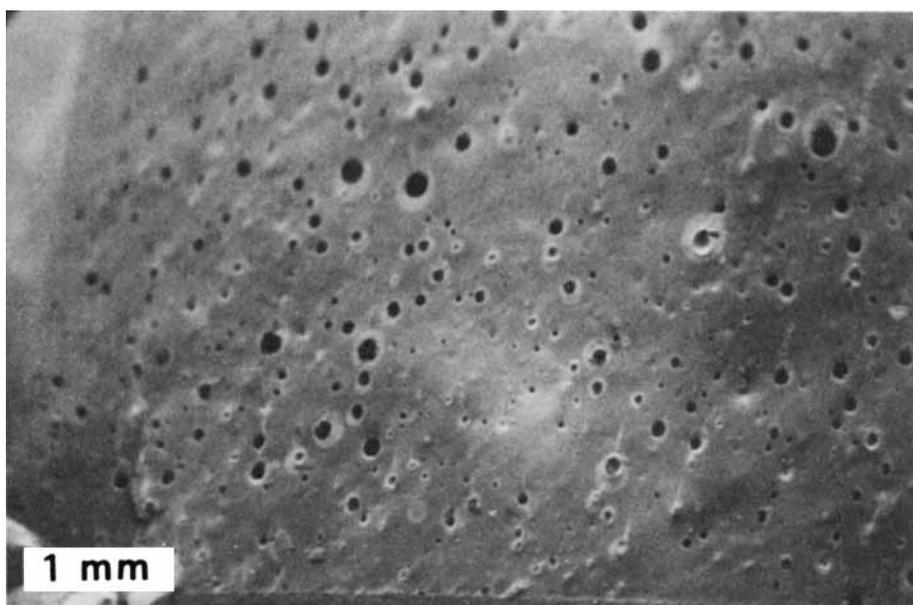
Resin-Thermoplastic Systems

The addition to the resin of moderate amounts of a thermoplastic, such as polystyrene (PS) or polyvinylacetate (PVAc), is known to reduce the shrinkage of the compound during crosslinking. From our measurements of linear shrinkage, additions of 10–15% weight of thermoplastic resulted in a practical zero shrinkage (from about 2% of the pure resin).

By the same additions, no particular changes were observed of the flexural modulus. In fact, thermoplastics like those normally used have a modulus similar to that of the pure resin, and no particular deviations are to be expected.

Drastic changes were instead observed in the flexural strength of the crosslinked systems, as it may be seen from the examples of Figure 2: By additions around 15% of PS or PVAc, the strength can be reduced to one-half.

This strength reduction can be largely influenced by the conditions in which the components are mixed together, transferred in the molds and crosslinked. The explanation is to be found in the morphological features of the system. In fact, the polymers currently used as thermoplastic additives are partially incompatible with the resin, so that a two-phase system is formed already in the liquid mixing of the components or in any case during crosslinking. This two-phase character has been recognized responsible for the low-shrink mechanism in the curing, due to a volume increase in the phase separation and/or to creation of voids in the globules of the prevailing thermoplastic dispersed



(a)

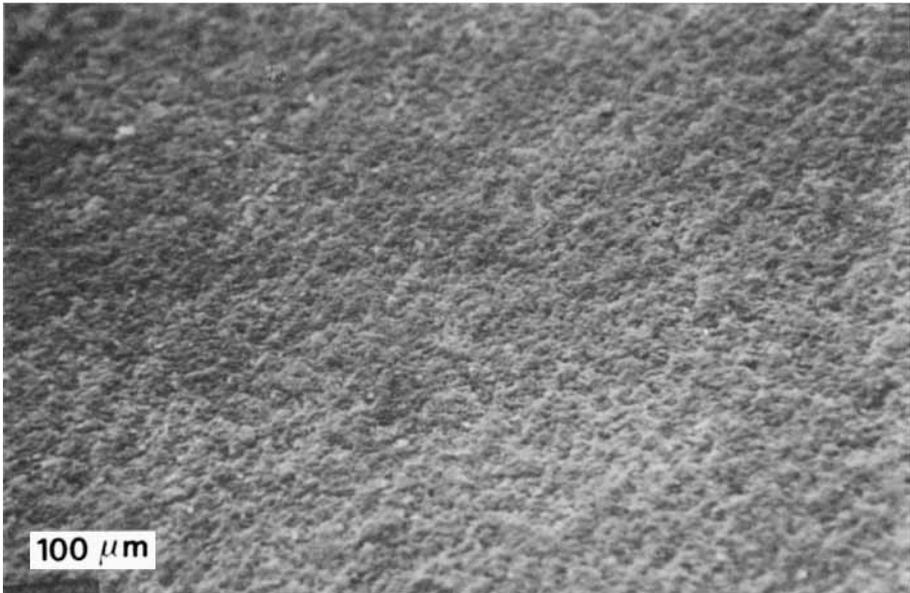


(b)

Fig. 3. SEM micrographs of the fracture surface morphology of samples of binary resin-thermoplastic systems: (a) resin + 7% PS; (b) and (c): magnifications of the same sample under (a), showing the prevailing thermoplastic inclusions; (d) and (e) resin + 7% PVAc at two different magnifications.



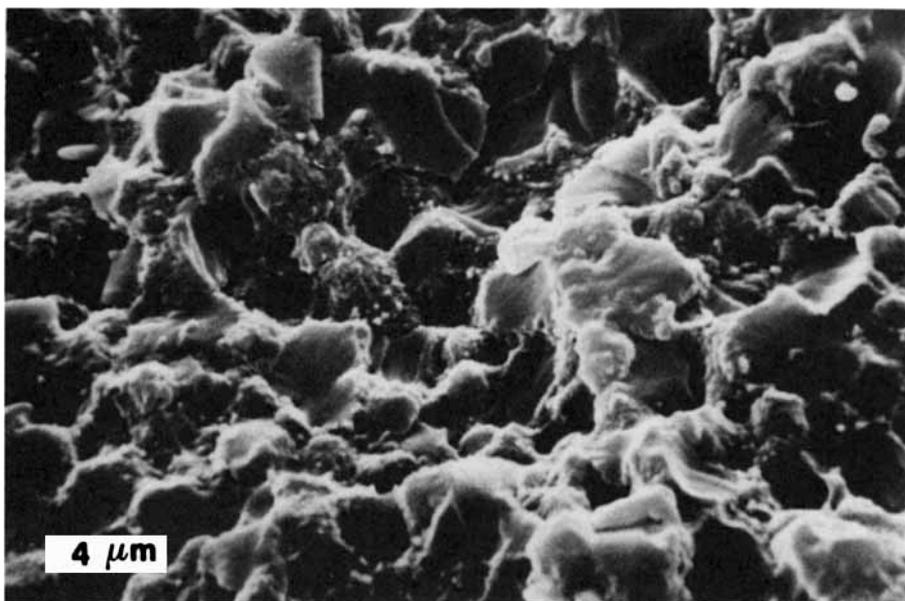
(c)



(d)

Fig. 3. (Continued from the previous page.)

phase.¹¹⁻¹⁶ The crosslinked system has therefore the structure of a particulate composite, with a relatively poor matrix-particles adhesion; this lowers the strength because of matrix area reduction and critical effects induced by the particles, whose dimensions are mainly determined by the mixing or sponta-



(e)

Fig. 3. (Continued from the previous page.)

neous phase separation variables. In Figure 2, two examples are given of the strength of resin-PS systems, the former starting with a fine liquid dispersion of the separated phase, and the latter with a coarser one.

This view is confirmed by the SEM micrographs of Figure 3. In particular, Figure 3(a) shows the fracture surface of a crosslinked mixture of resin and PS (7%), in which globules of the dispersed phase formed in the liquid mixing, prevailing consisting of PS and frequently containing voids, are clearly visible. Some of these globules are magnified in Figures 3(b) and 3(c). By contrast, in Figures 3(d) and 3(e) it may be seen, with two magnifications, the different morphology, with a much finer dispersion, of a crosslinked mixture of resin and PVAc (7%), for which the phase separation occurred during the curing.

Resin-CaCO₃ Systems

When CaCO₃ particles are added to the liquid resin, the viscosity of the suspension increases with the relative amount of filler. In Figure 4 an example is reported of the experimental dependence of the relative viscosity (the ratio between the actual viscosity η of the system and the viscosity η_0 of the pure resin) on the amount of CaCO₃ particles, expressed as volume fraction Φ . The relationship can be well described with the Mooney's equation¹⁷

$$\ln \frac{\eta}{\eta_0} = \frac{k_E}{1 - \Phi/\Phi_m} \quad (3)$$

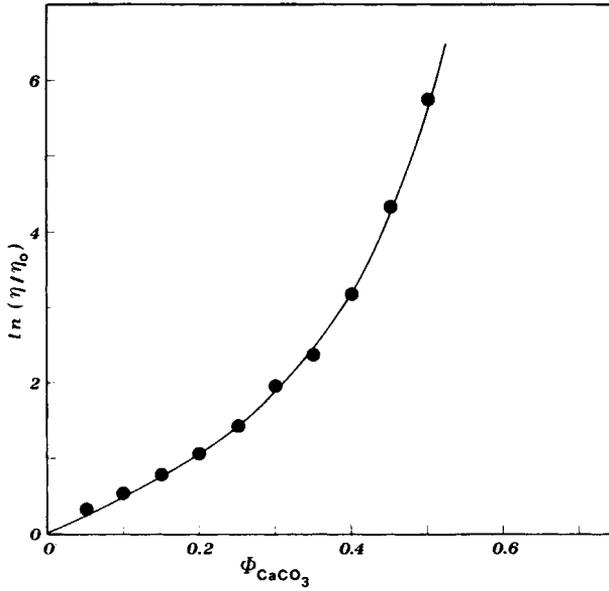


Fig. 4. Relative viscosity vs. CaCO_3 volume fraction of the uncured resin-filler system. Full line: Mooney eq. (3) with $K_E = 3.77$ and $\Phi_m = 0.76$.

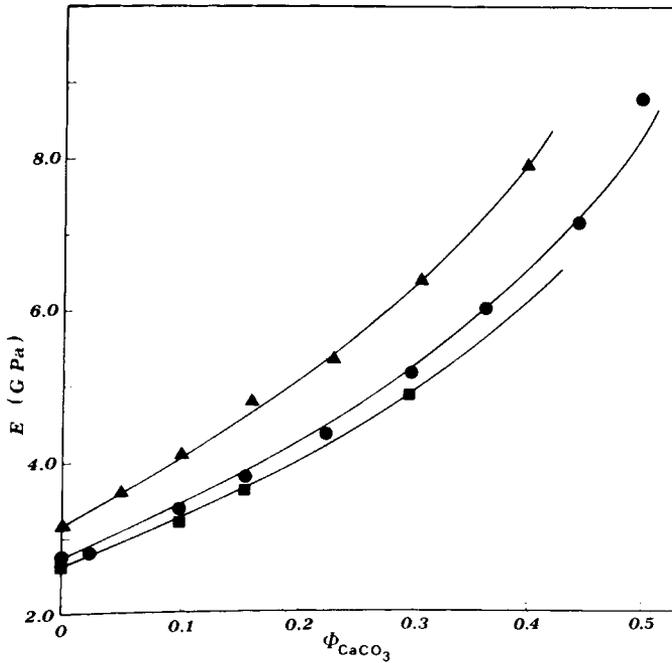


Fig. 5. Flexural modulus vs. CaCO_3 volume fraction of crosslinked binary or ternary systems: (●) resin; (▲) modified resin; (■) resin + 14% PS; (—) Halpin-Tsai eq. (4) with the following values of the parameters, respectively: $A = 1.40$; $B = 0.90$ (calcd.); $A = 1.80$; $B = 0.87$ (calcd.); $A = 1.34$; $B = 0.90$ (calcd.).

where k_E is the so-called Einstein's coefficient and Φ_m the volume fraction at the maximum packing of the particles. In Figure 4 the experimental points are well interpolated (—) by putting in the eq. (3): $k_E = 3.77$ and $\Phi_m = 0.76$, i.e., two parameter values that fall into a reasonable interval.¹⁸

Examples of the experimental relation between flexural modulus and filler content of crosslinked mixtures of resins and CaCO_3 are illustrated in Figure 5. The increase of the modulus is well fitted by some of the equations proposed so far, in particular by that of Halpin and Tsai¹⁹ (solid lines in Fig. 5):

$$E_{\text{rel}} = \frac{E_c}{E_m} = \frac{1 + AB\Phi}{1 - B\Phi} \quad (4)$$

Experimental results of flexural strength of the same crosslinked systems are reported in Figure 6.

For the system resin- CaCO_3 , the equation derived from the simplest "random model," based on the matrix area reduction of the fracture surface, with no adhesion between matrix and particles, and no critical effects induced by the filler,²⁰ for which the area fraction of the matrix equals its volume fraction²¹:

$$\sigma_{\text{rel}} = \frac{\sigma_c}{\sigma_m} = 1 - \Phi \quad (5)$$

(σ_c and σ_m = strengths of the composite and of the matrix) is surprisingly well obeyed, with an accuracy that cannot be found in the preceding literature. In Figure 7(a), an example of the morphology of a fracture surface clearly

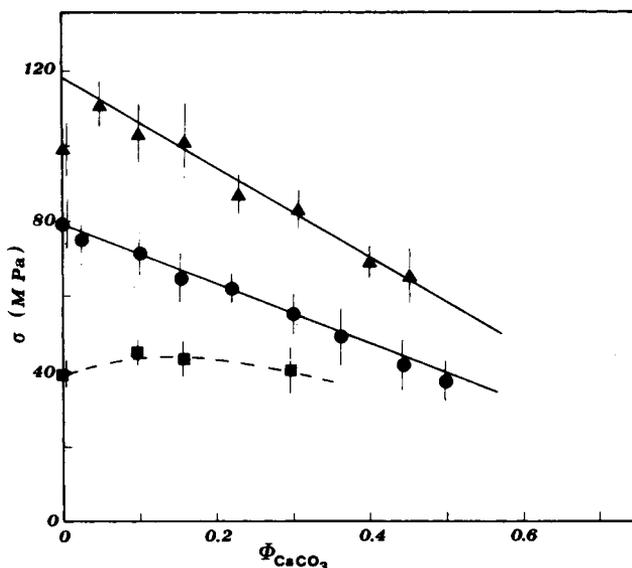
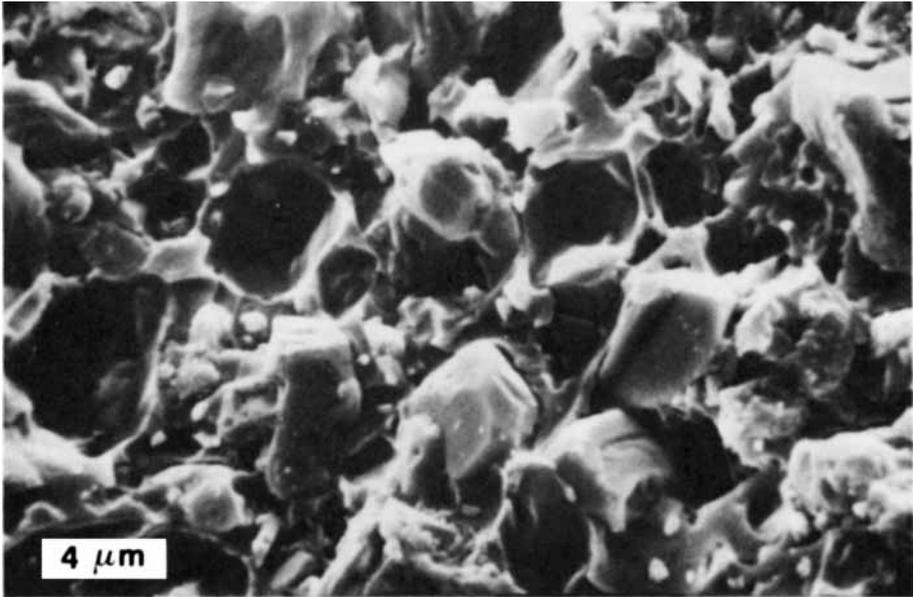
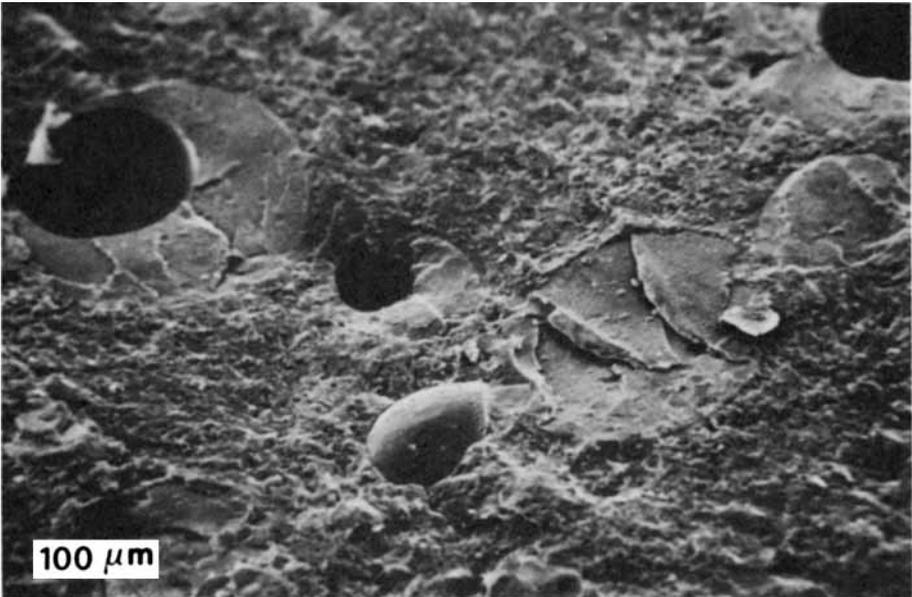


Fig. 6. Flexural strength vs. CaCO_3 volume fraction of crosslinked binary or ternary systems: (●) resin; (▲) modified resin; (■) resin + 14% PS; (—) eq. (5) (see text).



(a)



(b)

Fig. 7. SEM micrographs of the fracture surface morphology of samples of binary or ternary systems: (a) resin + 50% (vol) CaCO_3 ; (b) resin + 14% PS + 9.6% (vol) CaCO_3 .

evidences a pullout of the particles, which confirms the practical absence of adhesion to the matrix, at least at the breaking strains. An approximate evaluation of the critical flaw size of the matrix, according to the Griffith's theory using the experimental fracture quantities of the pure resin, gives a value of 30–40 μm ; comparable evaluations for polyester resins may also be found in literature: 22,²² 90,²³ and 38 μm .²⁴ Being the size of the particles in our case around 2–5 μm , i.e., decidedly smaller than that of the inherent critical flaw size of the matrix, it seems reasonable that the assumptions under which eq. (5) is derived can actually be satisfied in this case.

In the same Figure 6 are also reported results of a corresponding system with a modified resin, for which a moderate chemical interaction with CaCO_3 has to be expected. They show a quite unusual behavior, i.e., a clear increase of the strength in a first, very small filler fraction interval, followed by a linear decrease that can be described by Eq. (5) provided that a proper higher value for σ_m is taken into account (in this case $\sigma'_m = 1.19\sigma_m$). This behavior may be interpreted as a consequence of the formation of a stronger actual matrix material, due to a reaction of the resin with a limited amount of CaCO_3 during the mixing and crosslinking operations.

Figure 8 shows the results of the fracture toughness K_{Ic} of the same crosslinked systems as a function of the filler content. The values of K_{Ic} are similar for the two binary systems. They increase with the volume fraction of CaCO_3 up to a maximum or plateau value. This kind of dependence, different from a linear one, cannot be interpreted in terms of the onset of a transgranular fracture of the filler particles, as suggested by Moloney et al.²⁵ in the discussion of results with epoxy composites with different mineral particulate fillers, in that in our case the fracture micrographs invariably show dewetting of the CaCO_3 particles in the whole range of Φ investigated.

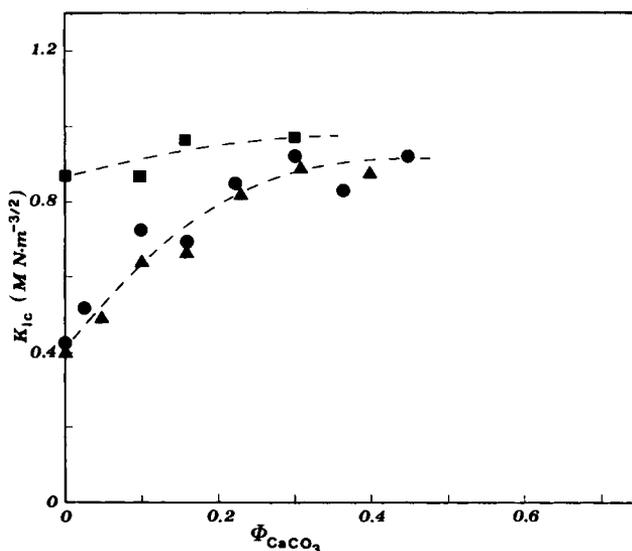


Fig. 8. Fracture toughness vs. CaCO_3 volume fraction of crosslinked binary or ternary systems: (●) resin; (▲) modified resin; (■) resin + 14% PS.

The corresponding values of the fracture energy G_{Ic} of the two binary systems, calculated from the experimental E and K_{Ic} values with the LEFM equation

$$G_{Ic} = \frac{(K_{Ic}^2)}{(E)}(1 - \nu^2)$$

are reported in Figure 9 ($\nu = 0.35$). Owing to a remarkable increase of the modulus with the addition of the filler, they show a wide maximum. A similar relation has also been observed in other cases of particulate composites.²⁵⁻²⁸

Resin-Thermoplastic-CaCO₃ Systems

When a thermoplastic polymer is added to the polyester resins, the mechanical properties of the resulting CaCO₃ particulate composites can be fairly different from those of the resin-CaCO₃ systems.

In Figures 5, 6, 8, and 9, some results may be seen of a ternary crosslinked system containing polyester resin, PS (14% of the total polymeric material), and CaCO₃. If compared with the results of the resin-CaCO₃ system, the modulus is slightly lower, but the strength is drastically reduced to values near those of the resin-PS system (Fig. 2). From the example of morphology reported in Figure 7(b), it may be observed that the particles of the substantially thermoplastic phase have a size decidedly larger than those of CaCO₃ (dispersed in the matrix background); reasonably they should induce critical

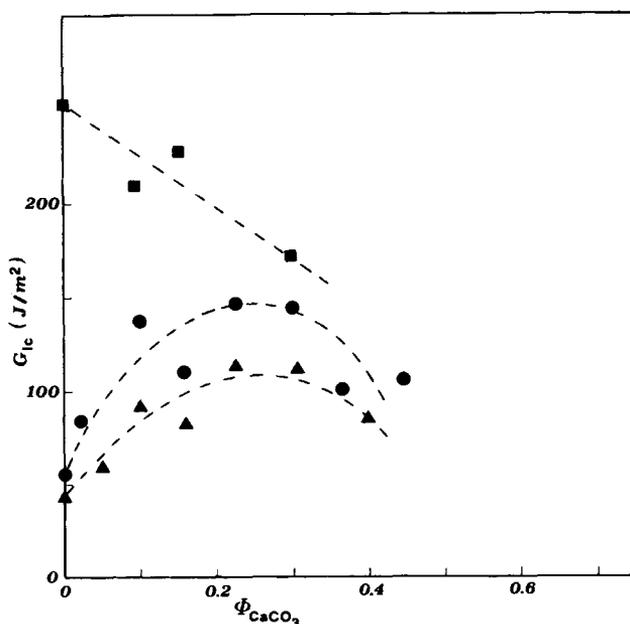


Fig. 9. Fracture energy vs. CaCO₃ volume fraction of crosslinked binary or ternary systems: (●) resin; (▲) modified resin; (■) resin + 14% PS.

flaws that dominate the fracture initiation and lower the system strength. The fracture toughness, on the contrary, is remarkably higher in the ternary system, without particular changes by increasing the CaCO_3 content (Fig. 8). Consequently, the pattern of G_{Ic} versus Φ (Fig. 9) is completely different from that of the binary systems, in that the fracture energy is drastically reduced by an increasing amount of CaCO_3 .

Particularly interesting are the results, reported in Figure 10, with the ternary system: modified resin, PVAc (7% of the total polymeric material), and CaCO_3 . The flexural strength follows a pattern clearly different from those of the preceding binary or ternary systems (Fig. 6), likely attributable to a noticeable adhesion between matrix and CaCO_3 particles. The fracture toughness and the fracture energy, which are similar for the binary systems modified resin-PVAc (at $\Phi = 0$ in Fig. 10) and resin-PS (at $\Phi = 0$, Fig. 8 and 9), undergo a remarkable decrease by increasing the CaCO_3 volume fraction.

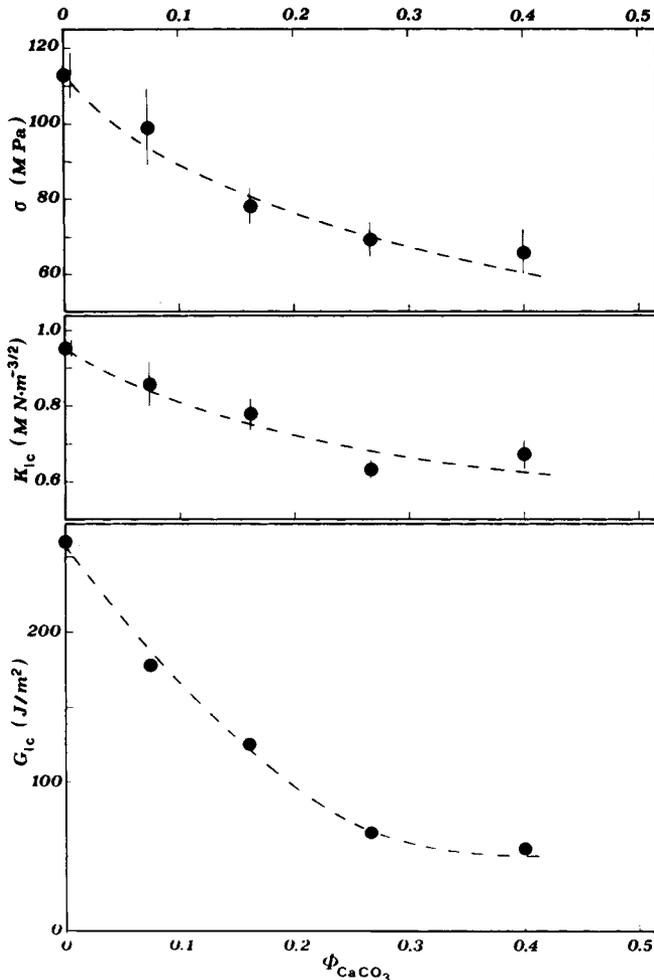


Fig. 10. Flexural strength, fracture toughness, and fracture energy vs. CaCO_3 volume fraction of the crosslinked modified resin + 7% PVAc + CaCO_3 system.

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