

# Polymer Composites Containing Plasma-Treated Mica.

## I. Flow and Mechanical Properties

H. P. SCHREIBER, and Y. B. TEWARI,\* *Department of Chemical Engineering*, and M. R. WERTHEIMER, *Department of Engineering Physics, Ecole Polytechnique, Montreal H3C 3A7, Quebec, Canada*

### Synopsis

Suzorite mica has been surface modified by microwave plasma treatment in ethylene gas. The surface-treated mica was used as a filler in polyethylene, polystyrene, and a mixture of these two polymers. Significant changes in rheological behavior ensue. These indicate that adhesion between polyethylene and irradiated mica is superior to that of interfaces using unirradiated mica. In contrast, ethylene irradiation reduces the ability of filled polystyrene compounds to store elastic energy in melt flow, an effect consistent with impaired adhesion at interfaces involving these components. An intermediate situation exists in the case of the two-polymer blend. The tensile properties of these systems also reflect surface treatment, reinforcement occurring in polyethylene-containing compounds, while the tensile properties of polystyrene composites deteriorate. Plasma-induced surface modifications of fillers to produce desired property changes in specified polymer matrixes are implied by the present work, but a fuller understanding of the chemistry of surface modification reactions is needed to substantiate these implications.

### INTRODUCTION

It is well known that flake particulates and fiber-shaped solids can be valuable reinforcing agents for a wide range of commodity polymers.<sup>1,2</sup> Adhesion at the polymer matrix-filler interface is one of the most important variables in the successful formulation of such filled polymer stocks, and a wide range of coupling agents (e.g., silanes) have been developed to promote this adhesion. Encapsulation of fillers by polymers synthesized on the reinforcing solids when these are used as catalyst supports in the polymerization is also a recognized route toward performance improvement,<sup>3,4</sup> but both of these methods are time consuming and tend to add significantly to the cost of reinforcement processes.

The recent development in these Laboratories of a large-volume (cold) microwave plasma (LMP) facility<sup>5</sup> has prompted attempts to modify the surface structure of typical reinforcement candidates (mica, wood fibers) by irradiating them in selected gas environments immediately prior to incorporating them into the polymer matrix. We believe that, as in low-pressure "glow"

\* Present address: Department of Chemistry, University of Manitoba, Fort Garry, Manitoba, Canada.

discharges,<sup>6,7</sup> the LMP treatment produces a thin, crosslinked polymer or oligomer sheath on the solid surface, the chemistry of this sheath depending on the "monomer" chosen for the irradiation process. In contrast to conventional surface conditioning procedures, effective LMP treatment is brief (generally of the order of seconds) and requires no contact of the solid with water or other suspending liquids. This at once simplifies the surface conditioning procedure and reduces the hazard of adding agents which may be deleterious to strong interfacial bonding. An earlier paper,<sup>8</sup> describing exploratory work, showed that the wettability of mica and wood fiber could be controlled by selecting the vapor in LMP irradiation and further showed that considerable control could be maintained over the tensile properties of composites formulated from irradiation-treated fillers in a polypropylene matrix.

The present papers (see also succeeding paper, referred to as part II in this work) report an extension of our work to filled systems involving LMP-treated mica, and polyethylene (PE), polystyrene (PS), and a 1:1 mixture of these thermoplastics. Individually, the polymers represent large-volume commodity resins in which reinforcement effects continue to be sought. In combination, PE and PS form an incompatible mixture<sup>9,10</sup>; property improvement through the addition of a compatibilizing filler would be valuable. Suzorite mica (Suzorite is trademark of Laviolette Mining Co., Montreal, Quebec) used in this work is an inexpensive flake reinforcer of growing appeal.<sup>1</sup> In addition to any gains to be realized in mechanical properties, mica is also capable of conferring useful dielectric effects to the composites (see also part II).

We limit ourselves in these reports to the study of effects arising from irradiating mica in ethylene gas. Our initial study showed<sup>8</sup> that significant changes in the wetting heats of mica resulted from such treatment, ostensibly because of the deposition of an olefinic polymer on the surface of the filler. A qualitative correlation between wettability and increased tensile strength of polypropylene composites further suggested that important changes were occurring in adhesion at the polymer-filler interface; this combination of factors seemed to justify the present extension of work.

## EXPERIMENTAL

### Materials

The following polymers were used in the present study: low-density polyethylene (manufactured by Canadian Industries Ltd) having a melt flow index<sup>11</sup> of 1.2 and a reference density of 0.919 g/ml; general-purpose polystyrene (of Dow manufacture) having an apparent molecular weight of  $8.2 \times 10^4$ , as calculated from the intrinsic viscosity in toluene<sup>12</sup> at 30°C.

To make the polymer blend matrix, equal weights of the two polymers were fused on a roll mill at 200°C with the addition of 0.1% thermal stabilizer (Santonox) and blended for 10 min. The blend was then ground down to fine fibrillar consistency and tumbled to ensure uniformity of composition.

Suzorite mica (a phlogopite mica with very low water content) was obtained from Laviolette Mining Co. (subsidiary of Marietta Resources International). The sample was wet screened to give a 40/60 mesh fraction. This was oven dried at 120°C for 48 hr prior to any further use.

## IRRADIATION SEQUENCE

Irradiation treatment of mica was conferred by the LMP apparatus described by Bosisio et al.<sup>5</sup> and also in our earlier publication.<sup>8</sup> Mica in 3- to 5-g quantities was placed in the rotating quartz tube of the apparatus and the unit was evacuated to a residual pressure of  $<10^{-3}$  torr. Ethylene gas was then metered into the apparatus to maintain a pressure of about 2.0 torr. The plasma discharge was struck by activating a constant-power (1.5 kW) 2.45-GHz microwave generator, and samples were treated for 30, 60, 90, 120, and 600 sec. Irradiation times exceeding 60 sec were attained in 30-sec bursts with 30-sec pauses between exposures, to minimize possible interference from excessive heating of the solid. Following irradiation, the reactor tube was flushed with dry nitrogen gas, and samples were stored under nitrogen in a desiccator for at least 48 hr before being incorporated in the polymer. The selected treatment conditions do not necessarily optimize the surface properties of mica relative to its use with the chosen polymers. For the present purpose, it seemed preferable to standardize as many of the irradiation variables as possible, in order to indicate clearly the effects of such surface treatment in the test case. The use of variable treatment times reflected the work of Hall and co-workers<sup>13</sup> and was intended to designate the range of treatment times needed (in this case) to produce measurable performance effects.

## COMPOSITES—PREPARATION AND PROPERTY EVALUATION

Composites of polymer plus 10% (wt) mica were formulated by adding the filler to fused stocks of the polymers in a Brabender Plasticorder. The Brabender was operated at 60 rpm and at 190°C for PE blends, while for PS and PS/PE mixtures, 240°C was the working temperature. Five-minute mixing was sufficient to generate a steady-state torque response, indicating uniform dispersion of the solid. The evidence of Woodhams and co-workers<sup>1,14</sup> shows that such melting reduces the aspect ratio of mica, hence reducing the magnitude of reinforcement effects, as also shown in part II. It is to be noted that powder compression molding gives superior results. Okuno and Woodhams have also shown<sup>14</sup> that loadings of up to 50–60% (wt) mica can be tolerated in polyolefin matrixes. Our choice of melt blending under rigorously uniform conditions was made for the sake of similarity with practical blending conditions. Although, as shown in the following paper, some reduction in particle size was incurred, the value of relative performance comparisons is not compromised thereby. Similarly, our purpose being to make comparative evaluations of treatment effects, the conservative choice of 10% loading level was made for experimental convenience.

Rheological properties (melt viscosity and extrudate swelling) of the blends were evaluated on the well-known gas-driven CIL High Shear Viscometer. In all experiments, the melt temperature was 190°C, and a single die with  $L/R = 11.36$  was employed. Since no die-entry or Robinowitch corrections<sup>15</sup> were applied, the data have a relative but not an absolute significance.

For mechanical and dielectric property evaluations (see also part II), plates were compression molded from blended stocks, using 190°C for PE composites and 240°C as the molding temperatures when PS was involved.

The Instron tester was used to measure stress-strain responses, shear moduli and ultimate tensile strengths being used as the performance criteria.

## RESULTS AND DISCUSSION

### Melt Effects

The effects of mica addition and LMP irradiation on rheological properties were evaluated from graphic representations of log apparent melt viscosity ( $\eta^*$ ) against log extrusion pressure and from the variation of postextrusion swelling ( $B$ ) with log extrusion pressure. The latter method follows evidence of Beynon and Glyde<sup>16</sup> that such representations are frequently well defined and linear. Typical viscosity results are shown in Figure 1 for the set of parent compounds. The relative influence of mica irradiation on melt properties is shown in Figures 2, 3, and 4 for PE, PS, and PE/PS compounds, respectively. In the ratio  $\eta^*/\eta_r^*$ ,  $\eta_r^*$  is the viscosity of the unfilled matrix polymer (Fig. 1). Treatment time is plotted logarithmically in Figures 2-4. For ease of comparison, the influence of unirradiated mica (treatment time = 0) is indicated on each  $y$ -axis. In each case, three levels of shear are reproduced, corresponding to extrusion pressures of 100, 500, and 1000 psi.

The flow curves of the parent resins (Fig. 1) follow expectations, each being a power-law fluid with substantial shear-thinning properties. At first sight, the behavior of the PE/PS blend is surprising. PE/PS mixtures are known to be incompatible in the melt,<sup>9,10</sup> a situation resulting in viscosities which can fall well below the values expected from simple combinatorial rules. It is

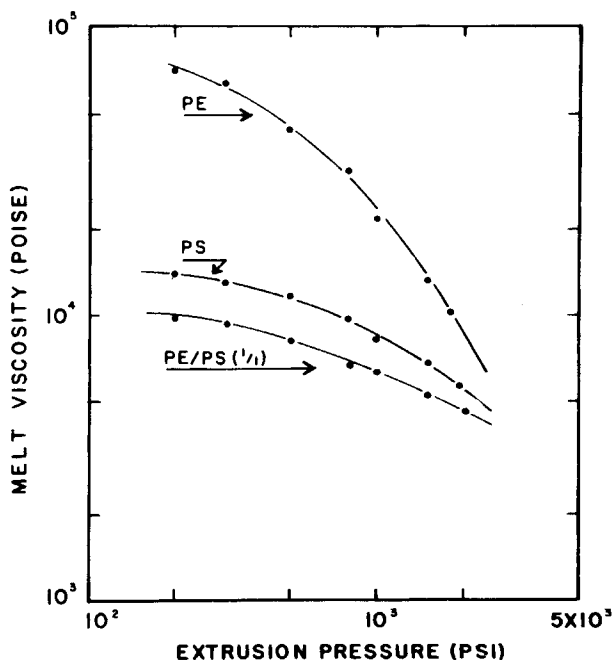


Fig. 1. Apparent viscosity-extrusion pressure relationships for three matrix polymers at 190°C.

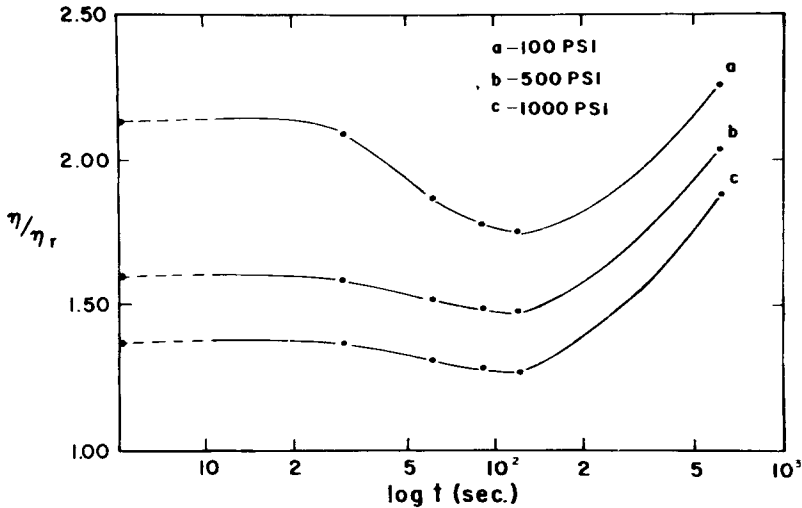


Fig. 2. Relative viscosity of mica-filled PE composites. Effect of irradiation time at three levels of extrusion pressure.

postulated that disruption of the entanglement networks of each polymer caused by the presence of the other accounts for the viscosity drop.

The presence of mica elevates the melt viscosity, as expected from the theory of particle suspensions.<sup>17</sup> The relative elevation tends to decrease with increasing shear, indicating shear-induced tendency for the solid to orient in the flow direction. In the case of PE (Fig. 2), the use of ethylene-irradiated mica initially reduces the viscosity rise and at the same time accentuates what we suppose to be the orientation effect. Such a response would be consistent with the deposition of an ethylenic polymer on the surface of the filler. Stronger adhesion at the polymer-filler interface would have an uncertain effect on the absolute viscosity of the composite but should promote the orientation of the flake, its motion closely coordinating with the orienta-

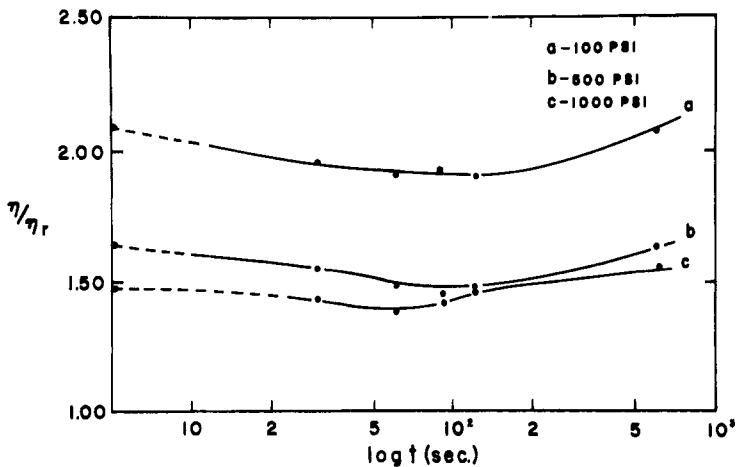


Fig. 3. Relative viscosity of mica-filled PS composites. Effect of irradiation time at three levels of extrusion pressure.

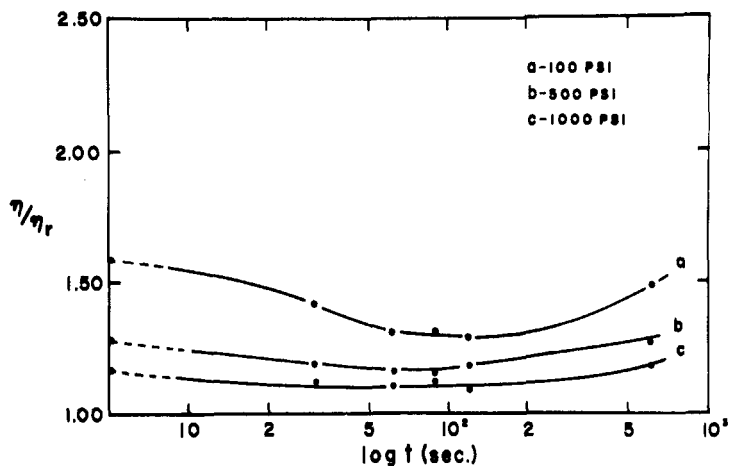


Fig. 4. Relative viscosity of mica-filled PE/PS composites. Effect of irradiation time at three levels of extrusion pressure.

tion of macromolecules in a shear field.<sup>18</sup> Optimum treatment time under the chosen conditions, from this standpoint, seems to lie around the 2-min mark. Extended irradiation (10 min), however, strongly increases the relative viscosity and suppresses orientation effects. Following the evidence of studies on glow-discharge treatments of solids,<sup>6,7,13</sup> a relatively thick, strongly crosslinked layer of polymer deposited by irradiation may be suspected in this case. Regions of melt surrounding such particles may be much more strongly bonded, forming viscous and relatively nondeformable domains within the melt structure.

In the case of PS (Fig. 3), the relative increment in apparent viscosity due to 10% mica addition is less pronounced, possibly because of poorer wetting properties at the PS/mica interface. The polymerization of an incompatible resin on the mica surface further inhibits interfacial adhesion, and neither the relative viscosity itself nor its shear dependence is a significant function

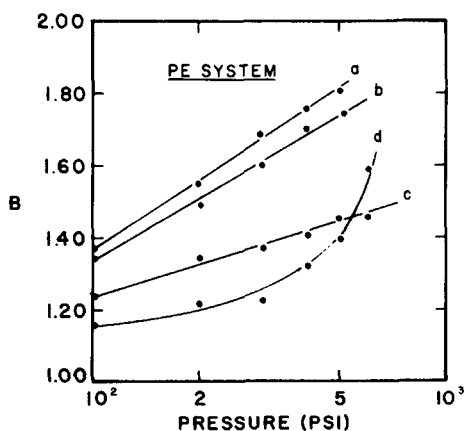


Fig. 5. Postextrusion swelling effects: (a) unfilled PE; (b) PE + 10% mica (no treatment); (c) PE + 10% mica (90 sec treatment); (d) PE + 10% mica (600 sec treatment).

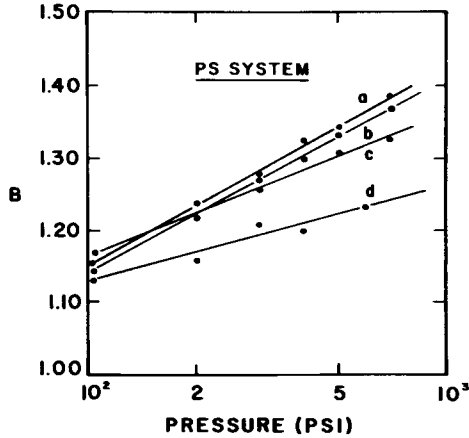


Fig. 6. Postextrusion swelling effects: (a) unfilled PS; (b) PS + 10% mica (no treatment); (c) PS + 10% mica (90 sec treatment); (d) PS + 10% mica (600 sec treatment).

of treatment time. As might be expected, an intermediate situation is apparent in Figure 4. Irradiation of mica presumably influences its interaction with the PE phase of the mixture as suggested above. The scatter of data in Figure 4 is more pronounced than in the other cases. This could well arise from local inhomogeneities in the PE/PS composition within the sample, accentuated by a tendency of the mica to associate preferentially with the PE component.

The influence of mica addition and of LMP irradiation on melt elasticity is given in Figures 5, 6, and 7; these present  $B$ -versus- $\log P$  data for the PE, PS, and PE/PS matrixes, respectively. The degree of postextrusion swelling is taken as a measure of elastic energy stored in the melt during extrusion,<sup>19</sup>

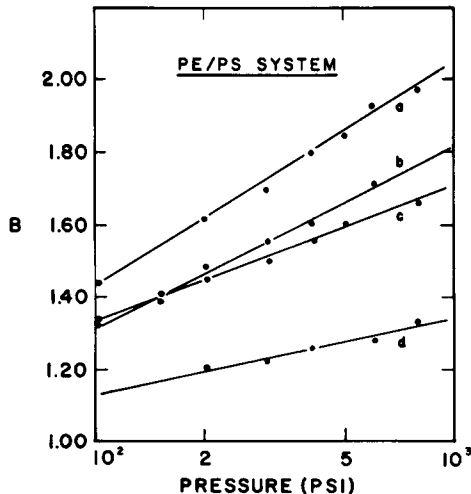


Fig. 7. Postextrusion swelling effects: (a) unfilled PE/PS mixture; (b) PE/PS + 10% mica (no treatment); (c) PE/PS + 10% mica (90 sec treatment); (d) PE/PS + 10% mica (600 sec treatment).

and the slope of the curves may be thought of as a swelling compliance ( $dB/d \log P = B_p$ ).

Curves a in Figures 5-7 represent extrudate swelling of the parent polymers, while the set labeled b are the reference swelling data for 10% composites with unirradiated mica. These data again follow expectations of earlier studies. Thus, the absolute level of die swell in the 50/50 blend is somewhat greater than the linear combination of the two components would predict. The effect is consistent with Han's findings on elastic properties of two-component melts.<sup>9,10</sup> We speculate as before that, due to the unfavorable wetting properties at PE/PS interfaces, the networks in domains formed by each polymer will tend to be more strongly bonded than would be the case in the pure materials. Each, therefore, becomes more elastic and generates an increased die-swell response than would normally be the case. It is interesting also that the critical shear stress for melt fracture<sup>19,20</sup> appears to be shifted upward in the PE/PS blend, rising to >800 psi from a value of about 550 psi for PE and approximately 700 psi for the PS component. Similar extensions of the laminar flow range in composite systems have been noted earlier.<sup>20,21</sup> The addition of unirradiated mica (curves b) lowers the  $B$  values, again disproportionately to the overall dilution of deformable polymer due to the presence of the inelastic filler. Newman and Trementozzi<sup>22</sup> have discussed this effect, noting its complexity and indicating that the presence of inelastic fillers alters the velocity profiles in melt flow. Significant "excess" changes in postextrusion swelling, therefore, are to be expected.

Curves c and d in Figures 5-7 show the behavior of composites with mica irradiated for 90 sec and 600 sec, respectively. The c series are representative of all irradiation times less than 600 sec, no significant experimental variation in  $B$  being detected over the entire pressure range when irradiation times of 30-120 sec were used. Ethylene LMP treatment is responsible for major decreases in the elastic responses of the three sets of composites, though probably for different reasons. In the case of PE and the PE/PS blend, the adhesion at PE/mica interfaces should be enhanced by the deposition on the solid of an ethylenic polymer. Exposure of the solid to vacuum may also contribute to enhanced adhesion. At this time, we are not able to evaluate this contribution quantitatively, but the PS results indicate it to be of secondary importance. The irradiated mica should, therefore, function as a stabilizer of entanglement networks in PE domains, reducing the swelling compliance and elevating the shear stress needed for significant "yielding" of crosslinks in the network structure. Curve d, Figure 5, is particularly pertinent in this regard. The melt strength of this material is sufficiently great so that virtually no swelling increment is observed up to 300 psi. Thereupon, curve d strongly resembles the swelling response of such melts as linear PE or lightly crosslinked network polymers<sup>16,21</sup> (e.g., EP rubber and similar elastomers). The implication is that the bond strength at polymer/filler interfaces is great enough to simulate the properties of polymers with much higher crosslink densities than are inherent in low-density PE.

The PS system responds more simply (Fig. 6). Here, we may postulate that the dispersed filler made more incompatible by the irradiation treatment, restricts the dimensions of networks. In contrast to the PE case, these melts become weaker owing to the addition of mica, the effect becoming par-



TABLE I  
Effect of Mica on Tensile Properties of Compounds<sup>a</sup>

Polymer property	PE		PS		PE/PS	
	Modulus $\times 10^{-5}$ , psi	T.S. $\times 10^{-3}$	Modulus $\times 10^{-5}$ , psi	T.S. $\times 10^{-3}$	Modulus $\times 10^{-5}$ , psi	T.S. $\times 10^{-3}$
Unfilled polymer	1.02	3.9	5.76	7.2	1.33	2.8
Unirradiated mica	1.36	4.1	6.06	5.9	0.96	1.8
60-Sec mica	1.55	4.5	5.70	5.9	1.37	2.5
90-Sec mica	1.62	4.7	5.33	5.7	1.44	2.7
120-Sec mica	2.07	5.1	5.53	6.2	1.76	3.1
600-Sec mica	2.49	5.5	5.01	5.4	1.92	3.3

<sup>a</sup> Filled polymers contain 10% (wt) mica. Tensile strength of mica  $\approx 35 \times 10^3$  psi.

ticularly pronounced following the longer treatment time of 600 sec. These speculations would call for a complex, intermediate situation to arise in the PE/PS mixture (Fig. 7), with appreciable reinforcement of PE domains and more effective separation of PE and PS domains. The elastic response of such a system is, expectedly, complex. The data in Figure 7 are not inconsistent with such complexity, but neither are they sufficiently discriminating to allow further clarification of the situation. The implied ability either to enhance or restrict the melt strengths of filled composites through LMP treatment, however, clearly warrants more detailed experimentation. This is now in progress.

### MECHANICAL PROPERTY EFFECTS

Ultimate tensile properties and tensile moduli of the materials used in this study are reported in Table I. The tabulation amplifies the discussion points raised above and indicates a satisfying degree of internal consistency between rheological and solid-state effects arising from the use of LMP-irradiated mica.

The addition of untreated mica to the pure polymers leads to mild reinforcement, the moduli increasing by about 30% in the case of PE and by some 5% for PS. The tensile strength of PE is practically unchanged, but a significant loss of tensile strength occurs in PS. Neither modulus increment matches expectations of Halpin-Tsai theory,<sup>23</sup> and the lack of useful aspect ratio data does not permit calculations of Padawer and Beecher's modulus-reduction factor.<sup>2</sup> There is no reason to believe that this factor would change in going from a PE to a PS matrix, however, and the superior relative performance of the PE compound can again be taken as suggestive of stronger adhesion at PE/mica than at PS/mica interfaces. Untreated mica is of no help to the tensile properties of PE/PS; presumably, the solid only provides additional points of discontinuity which are not effective as stress-bearing centers but may, in fact, provide loci for stress release.

The LMP treatment of mica in ethylene has sharply different, but important, effects on all three of the polymer matrixes. As already suggested, increasingly effective adhesion at PE/mica contacts eventually more than doubles the tensile modulus. Taking the tensile strength of mica as 35,000 psi and its density as 2.7 g/ml (supplier's data, see also ref. 1), the strengths of

composites with 120- and 600-sec mica are in good agreement with calculations based on the use of volume fractions of the materials.<sup>23</sup> Moreover, performance continues to improve with treatment time, in keeping with preceding postulates of improving adhesion as the ethylenic polymer layer at the mica surface is more fully developed. In terms of the tensile properties of PS composites, the mica treatment is obviously harmful. The PS/PE case is difficult to interpret in detail, but the moderate increase in modulus and tensile strength values upon LMP irradiation is consistent with the supposition that the mica promotes effective separation of PE and PS domains and at the same time acts as a proved reinforcing agent for the PE component.

## CONCLUSIONS

Microwave plasma irradiation of mica using ethylene gas has led to surface modifications which alter significantly the role played by the solid when added to PE, PS, and PE/PS matrixes. Rheological and mechanical property test determinations indicate that important improvements have been produced in PE and to a lesser degree in a PE/PS mixture, while the properties of PS compounds are inferior to those using unirradiated mica. It, therefore, appears possible to design surface-conditioning procedures which will lead to desired property changes in composites based on specified polymer matrixes. In order to optimize such procedures, an understanding of the chemistry of irradiation processes is desirable. This represents objectives for future research in this field.

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