

# Preparation and Characterization of Perlite-Filled High-Density Polyethylenes. III. Impact Properties

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## SYNOPSIS

Impact properties of perlite-filled high-density polyethylene (HDPE) composites were studied with the Charpy method by using both notched and unnotched samples.  $\gamma$ -Aminopropyltriethoxy silane ( $\gamma$ -APS, A-1100) was used as a silane coupling agent to improve the interfacial adhesion. The influences of the molecular parameters of HDPEs, molecular weight, degree of branching, degree of crystallinity, and also the effect of  $\gamma$ -APS on the impact properties are represented in this work. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Although the addition of particulate fillers into thermoplastics increases stiffness and hardness, fracture properties of the composites usually deteriorate.<sup>1,2</sup> As mentioned by Friedrich and Karsch<sup>3</sup> when thermoplastic polymers orientate or crystallize with strain, they often show enhancements in tensile yield strengths with most fillers, at least at lower filler concentrations. On the other hand, they exhibit poor bonding with most mineral fillers. Hence, they are able to separate and deform away from the filler surface (to stretch and work harden). In a fracture process, the matrix stretching generally requires a large amount of energy, whereas the energy required for the formation of voids and cracking at the interface between the polymer and the filler is considerably smaller. For these reasons, the addition of fillers usually causes a reduction in the fracture properties.<sup>4</sup>

The important parameters affecting the fracture strength of composites are polymer and filler characteristics, volume fraction of the filler, and the interfacial adhesion between polymer and filler.<sup>1,3</sup> The interfacial adhesion influences the fracture properties in a more complex way than the other me-

chanical properties, that is stress, strain, and modulus.<sup>1</sup> Silane coupling agents are added to polymer-filler systems to improve the interfacial adhesion and consequently the mechanical and other physical properties of the composites such as flow and thermal properties.<sup>5</sup> However, the effect of using these agents on the impact properties is not clear as yet. In some studies, it was found that increasing the adhesion between the polymer and the filler with silane coupling agents led to decreases in the maximum crack growth resistance in mica-filled polypropylene (PP)<sup>6</sup> and glass flake PP composites.<sup>7</sup> On the other hand, some silane coupling agents might modify polymer properties in the interphase region, through interpenetrating polymer networks, thus providing greater toughness to the composite as was shown in silane treated glass flake PP composites.<sup>5,8</sup>

The aim of this study, which is the last part of our work,<sup>9,10</sup> is to investigate the impact properties of perlite-filled high-density polyethylene (HDPE) composites considering the type of PE, the filler concentration, and the effect of a silane coupling agent.

## EXPERIMENTAL

The blending of filler, treated and untreated perlite, with HDPEs was described in our previous work.<sup>9-11</sup> Silane coupling agent,  $\gamma$ -aminopropyltriethoxy silane ( $\gamma$ -APS) (Union Carbide), was applied to perlite.

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For the impact tests, the composites were compression molded in specially prepared molds. Nine samples at a time (dimensions  $0.75 \times 0.4 \times 6.0$  cm), were molded at  $200^\circ\text{C}$  under  $1400 \text{ kg/cm}^2$  pressure and then cooled by circulating tap water, after the temperature was allowed to drop below  $175^\circ\text{C}$ .

The impact tests (notched or unnotched) according to ASTM-D256-78, Charpy method, were carried out by using a Plastics Impact Machine (type H20) at room temperature. The V-shaped notch depth was 1.3 mm and notch tip radius angle  $22.5^\circ$ . Impact strength values were given in terms of kN/m. The averages of 10 measurements are shown in the figures.

## RESULTS AND DISCUSSION

Figure 1 (a–d) represents the variation of impact strength with the treated and untreated perlite content in HDPE composites for both notched and unnotched samples. The deviation from the average of the 10 measurements of impact tests are shown as scatter bands in Figure 1. The scatter becomes smaller with silane coupling agent treatment and increasing perlite concentration in composites. The variation of impact strength values for the composites can also be followed from the area under the stress–strain curves given in our previous work.<sup>9</sup>

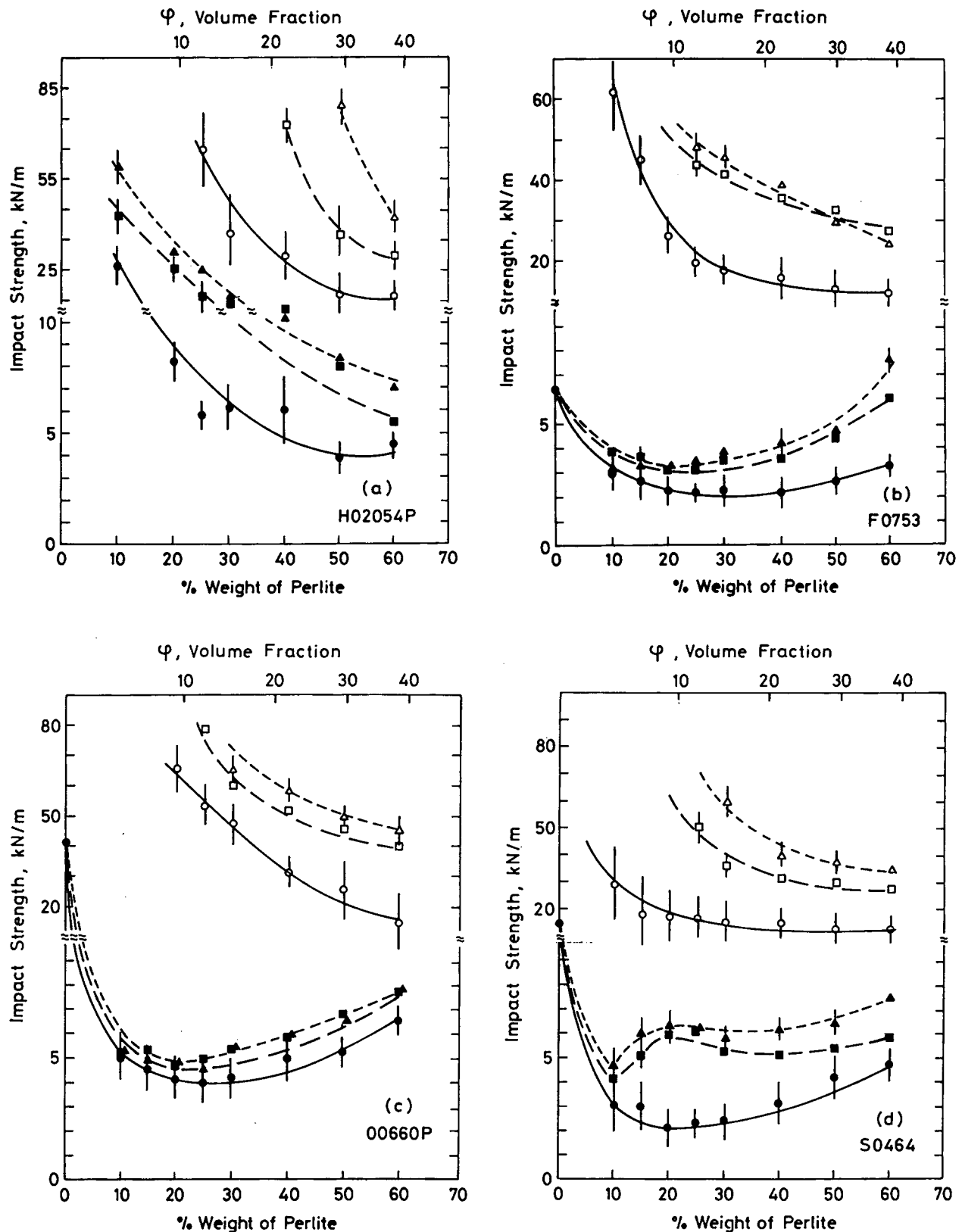
The impact strength of unnotched samples of H02054P [Fig. 1(a)] and 00660P [Fig. 1(c)] containing untreated perlite were not measurable up to 25 and 20% perlite respectively, that is, the samples did not break. On the other hand, brittleness (i.e. fracture) in the other two sets [Fig. 1(b,d)] was observed at 10% loadings. Impact strength decreased as the amount of perlite increased for H02054P and 00660P composites. However, for the branched PE, F0753 and highly crystalline, low molecular weight PE, S0464, impact strength values remained almost constant for higher filler concentrations after certain loadings of filler (20–30%).

Notching did not greatly change the impact behavior of H02054P composites [Fig. 1(a)]. The impact strength decreased as the untreated perlite concentration increased. Upon notching, we followed the variation of impact strength starting from the first loading of perlite, 10%. In the notched samples of other PE composites [Fig. 1(b–d)], after a sudden reduction in impact strength at 10 wt % of untreated perlite compared to the unfilled polymers, impact strength improved slightly with increased perlite concentration. This indicates that fracture toughness (or ductility) increases at high concen-

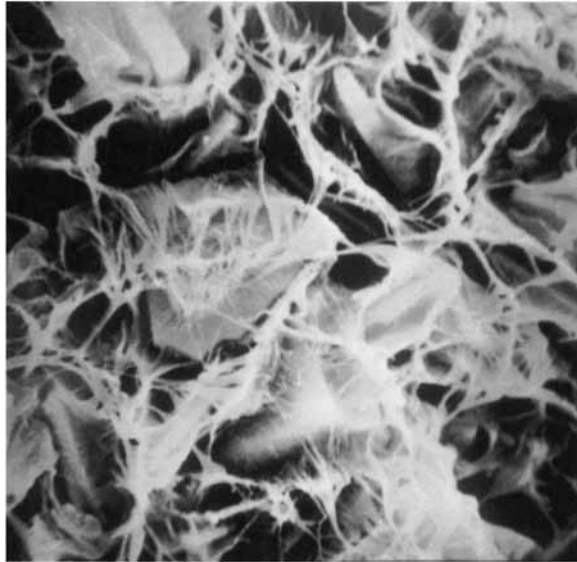
trations of perlite in the presence of a defect (crack). This effect of the filler (perlite) could be expected to be more important for materials that exhibited strong notch sensitivity, as in the case we observed in HDPE. Similar results have been obtained at low concentrations (< 20 wt %) of mica filled PP composites.<sup>4</sup> For H02054P, there was no improvement in impact strength in the presence of a defect with increased concentrations of perlite. This was possibly the consequence of its high molecular weight compared to others. As discussed in the flow properties of the perlite filled HDPEs, there were mixing difficulties in H02054P due to its high molecular weight and melt viscosity.<sup>10</sup> This may have caused increased void formation that in turn influenced the impact strength. It can be concluded that high molecular weight (highly viscous) PE H02054P, seems to be notch sensitive compared to others. In other words, notch and unnotched samples of H02054P exhibit the same trend. However, in general, ductility of the composites gradually decreased with the amount of perlite.

$\gamma$ -APS treatment resulted in higher impact strength for all types of PEs and at all concentrations of perlite. The impact strength values of unnotched composites were not measurable up to 40 and 50% perlite for H02054P, 25% for F0753, 25 and 30% for 00660P, and 25 and 30% for S0464 composites, when perlite was treated with unhydrolyzed and hydrolyzed  $\gamma$ -APS, respectively. This improvement in impact strength with the application of silane coupling agent can be attributed to the reduction in the void formation due to enhanced interfacial adhesion.

Through Figures 2–7, the electron microscopy of the fractured surfaces are represented in order to visualize the adhesion between the perlite and PEs. Hydrolyzed  $\gamma$ -APS treatment enhanced the adhesion between perlite and H02054P PE (Fig. 2) that shows the fractured surface of the H02054P sample at 50% perlite loading. Despite the further increase in interfacial adhesion with silane coupling agent, the high molecular weight H02054P displayed a decrease in impact properties with the amount of filler for both notched and unnotched samples. Yet, the hydrolyzed silane treated H02054P composites became less ductile after higher perlite loading compared to dry silane treated and untreated ones. In the notched samples of F0753, 00660P, and S0464 composites the increase in impact strength at higher concentrations of treated filler may indicate a decrease in void formation in the presence of a coupling agent and also the enhancement of ductility in the presence of a defect. This enhancement in hydro-



**Figure 1** The variation of impact strength with the amount of perlite for HDPE composites, (a) H02054P, (b) F0753, (c) 00660P, (d) S0464. Symbols used are: (—○—) untreated perlite, (—□—) dry silane treated perlite, and (—△—) hydrolyzed silane treated perlite. Open symbols are for unnotched samples and filled symbols are for notched samples. The corresponding volume fractions in terms of percentages are given above the figures. The scattering band is shown on the data points if the deviation is higher than 5% of the average.



**Figure 2** Scanning electron micrograph of 50% hydrolyzed silane treated perlite-H02054P composite, the impact fractured surface.



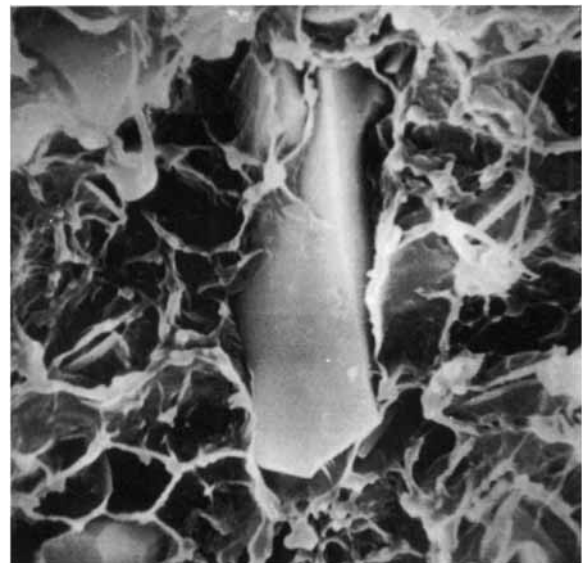
**Figure 4** Scanning electron micrograph of 50% hydrolyzed silane treated perlite-F0753 composite, the impact fractured surface.

lyzed  $\gamma$ -APS treated perlite at 60% for F0753 PE, is so high that the impact strength is greater than that of the pure PE. The difference between the treated and untreated perlite composites for F0753 can be seen in the fractographs in Figures 3 and 4. The strong adhesion results in all the perlite particles being covered by a microdrawn PE matrix and is clearly seen in Figure 4 compared to untreated

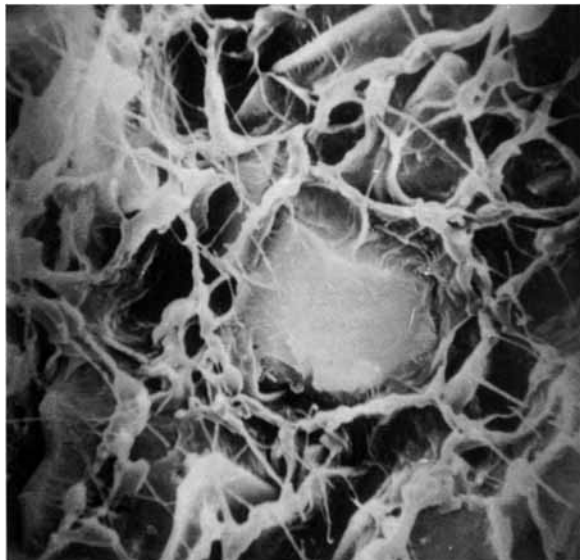
perlite in Figure 3. For dry silane treated perlite, this value is quite close to pure PE. Similar cases were observed and suggested for mica/PP composites.<sup>4,12</sup> The increase in impact strength for S0464 composites, in the presence of  $\gamma$ -APS, after a reduction at 10%, reached a maximum at 20% perlite concentration. This may be attributed to the net-



**Figure 3** Scanning electron micrograph of 50% untreated perlite-F0753 composite, the impact fractured surface.



**Figure 5** Scanning electron micrograph of 25% untreated perlite-S0464 composite, the impact fractured surface.



**Figure 6** Scanning electron micrograph of 25% hydrolyzed silane treated perlite-S0464 composite, the impact fractured surface.

work formation of polymer chains (by microdrawing) that easily distributes the impact energy to the whole sample by the strong adhesion. This is shown in Figures 6 and 7.

The effect of types of PEs on impact behavior is shown in Figure 8(a-c). It was observed that H02054P and 00660P were tougher than S0464 and F0753 composites. As given in Part I of this work,<sup>10</sup> elongation at break values of H02054P and 00660P composites were found to be higher than the other PE composites indicating that H02054P and 00660P composites were tougher and more ductile than the others. Indeed the impact strengths also indicate the same fact. Although the impact strengths of PE composites are well separated from each other due to their inherent properties, at high concentrations of filler (50 and 60%), the impact strength of the unnotched composites come close to each other, and this condition is not affected by the silane treatment. However, in the notched samples of the composites, the impact strength values are well separated even at high perlite concentrations except for the hydrolyzed silane treated ones. Yet, the increasing concentration of filler appears to minimize the difference between the impact strength of PEs in particular unnotched samples.

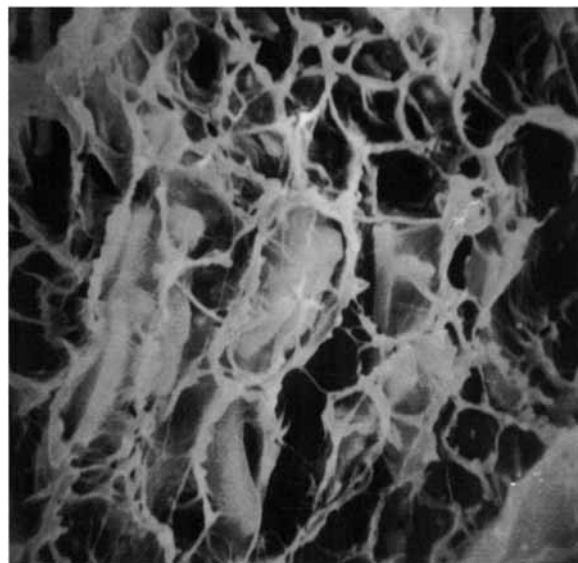
In addition to these improvements in yield strength, tensile strength, elongation at break, elastic modulus,<sup>9,11</sup> and thermal and flow properties,<sup>10</sup> the enhancement of the fracture performance in silane treated perlite composites is further substantial

evidence for the improved adhesion. Scanning electron micrographs supplied here and previously,<sup>9</sup> improvements of impact strength, yield stress,<sup>11</sup> and elongation at break<sup>9</sup> show that  $\gamma$ -APS modifies the interphase region of perlite-HDPE composites, with the possible formation of "pseudo interpenetrating polymer networks." Similar results were previously suggested by Plueddemann<sup>5</sup> for amine silanes in polyolefins.

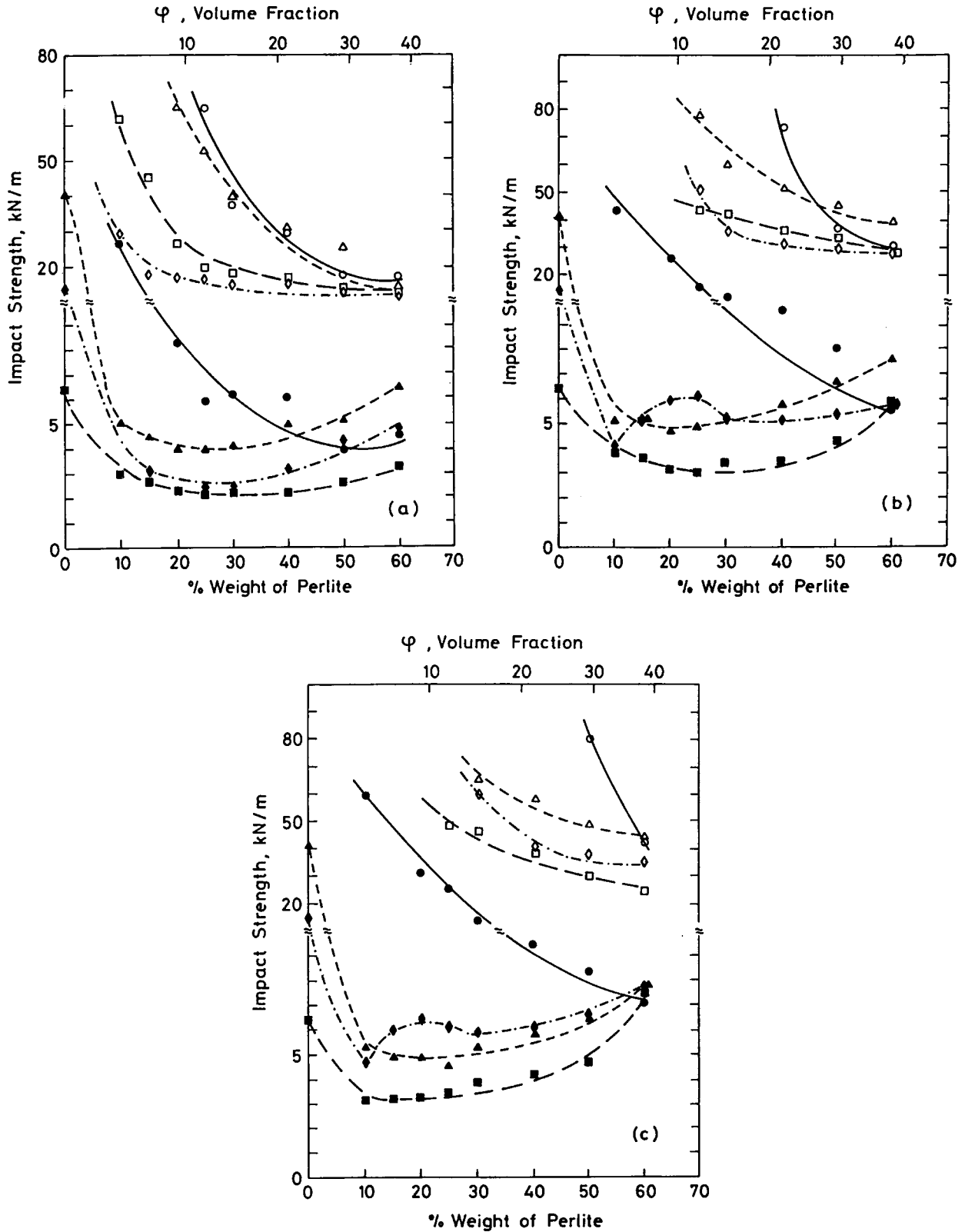
The improvements in yield stress,<sup>11</sup> elongation at break,<sup>9</sup> (Part I) and impact strength of perlite filled PEs indicate that composites become more ductile and tough in the presence of a coupling agent. However, ductility is lost in untreated perlite composites above a certain filler concentration and the samples become more brittle regardless of the type of PE.

## CONCLUSIONS

The branched PE, F0753, and high crystallinity, low molecular weight PE, S0464, composites have lower impact strengths than the other PEs, H02054P and 00660P. In addition to a sudden decrease in elongation at break with increasing perlite concentration,<sup>9</sup> the lower impact strength values for F0753 and S0464 indicate that these two composites are less ductile (or more brittle) than the other PEs.  $\gamma$ -APS treatment improves impact strength for all cases. The improvement of impact strength in the



**Figure 7** Scanning electron micrograph of 40% dry silane treated perlite-S0464 composite, the impact fractured surface.



**Figure 8** Comparison of impact strength of perlite-HDPE composites: (a) untreated perlite-filled composites; (b) dry silane treated perlite-filled composites; (c) hydrolyzed silane treated perlite-filled composites. (—○—) H02054P, (—□—) F0753, (—△—) 00660P, (—◇—) S0464. Open symbols are for unnotched samples and filled symbols are for notched samples. The deviation can be followed from Figure 1.

presence of the coupling agent shows the enhancement of toughness and ductility and also may be evidence for the formation of pseudo interpenetrating polymer networks at the interphase when fillers are treated with  $\gamma$ -APS in HDPE composites. Indeed, the presence of microdrawn PE on the surface of filler provides the fracture toughness in  $\gamma$ -APS treated perlite.

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