Preparation and Characterization of Perlite-Filled High-Density Polyethylenes. I. Mechanical Properties

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SYNOPSIS

Four different types of high-density polyethylenes (HDPE) were blended with perlite at different concentrations. Silane coupling agent γ-aminopropyltriethoxy silane (γ-APS, A-1100) was used to enhance the adhesion between perlite and HDPEs. Ultimate tensile strength and elastic modulus increased as the perlite content increased, while ultimate elongations decreased with the increasing amount of perlite. Exceptional variations in the measured properties are explained in terms of the differences in polyethylenes used in the composites. The biggest improvement in ultimate tensile strength was observed in the highly crystalline polyethylene; on the other hand, in the absence of silane coupling agent the high molecular weight polyethylene showed the least improvement in tensile strength. The effect of branching in HDPE composites was demonstrated. The enhancement of interfacial adhesion by using a coupling agent was also examined by scanning electron microscopy (SEM). © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical and other characteristic properties of composites are vital for designing materials, and the prediction of these properties from the filler and matrix properties has considerable importance. Filler characteristics such as type of filler,[1-5] size and size distribution,[6,7] shape,[1,4,5,8] and concentration[1-11] have been shown to affect the mechanical and other properties of the composites. Polymer characteristics influencing the mechanical properties of the composites can be summarized as molecular weight,[12] degree of branching or crosslinking,[2] and crystallinity and morphology.[12,13]

Regarding the variation and enhancement of the mechanical properties in a composite material, the key point is the interfacial adhesion between the matrix and the filler. The most crucial factor which directly influences the mechanical properties is the strength and the weakness of the load transfer between the polymer and the filler and, therefore, the interfacial adhesion. By using certain coupling agents which promote the adhesion between two different materials, the interaction can be improved and optimum mechanical properties can be achieved.[14,15]

In some cases, the mechanical properties of the composites can be predicted from basic principles. However, sufficient knowledge about polymer–filler interaction does not exist; hence, to determine the property changes, experimental methods are generally used. These properties are generally modulus, ultimate properties, yield stress, impact strength, and flexural properties.

Modulus, which is a bulk property, depends primarily on the geometry,[4,5] particle size,[6,7] and concentration[1-7,9-12] of the filler and can be described by several equations.[16-20] In general, modulus (stiffness) increases with the addition of filler because flexing of the matrix is prevented by the relatively high modulus filler particles.

By definition, the ultimate tensile strength of composites is described as the maximum achievable stress at the corresponding strain.[21] Since fracture mechanisms are complex, a theoretical study on tensile strength becomes very difficult. The prediction of tensile strength requires modes of failure,

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the character of polymer–filler adhesion, distribution of filler particles, perfection of alignment, particle size, shape, and the brittle and ductile nature of materials, in addition to ultimate stresses and strains of the matrix.[22] If there is adhesion between polymer and filler, tensile strength of the composite increases; in other cases, if there is weak or no adhesion, tensile strength decreases.[1] It has been shown that a modest degree of reinforcement by dispersing stress more effectively depends on the rigidity of matrix (polymer) and filler at low filler concentrations; however, at higher filler concentrations due to the decrease in matrix continuity, a loss in tensile strength is observed.[23]

Inorganic fillers such as glass,[5,8,24,25] mica,[6,9–11,26] $CaCO_3$,[2,4,12] and silicates (talc and wollastonite)[1,2,5,7] are among the widely used particulate fillers in different polymeric matrices. Perlite, however, a volcanic silicate found freely in nature, has received little attention in the polymer field as a filler and reinforcing material.[27–29] The chemical composition of perlite appears to be quite similar to glass (see Table II). Among the works mentioned, polyethylene–filler composites occupy only a small fraction of the literature; e.g., kaolin,[3] talc,[2] $CaCO_3$,[3,12] mica,[26] and glass[8,24,25] are the most common fillers used in polyethylene composites.

In this work, perlite was used as a filler in HDPE matrices differing in molecular weight, degree of branching, degree of crystallinity, and melt flow index. To enhance the interfacial adhesion, silane coupling agent γ-aminotriethoxy silane (γ-APS) was applied to the filler by two different methods, i.e., from ether and from aqueous solution. The first part of this work represents and discusses the effects of molecular parameters of polyethylenes, perlite concentration, and also the influence of γ-APS treatment, on the ultimate mechanical properties of HPDE composites. In Parts II and III the flow, thermal, and impact properties are considered.

EXPERIMENTAL

Materials

Four types of HDPEs with different properties, coded H02054P and 00660P, were supplied in powder form from BP Chemicals, UK. Other polyethylenes, coded S0464 and F0753, were supplied in granular form from Turkish Petrochemical Industry, Petkim, Aliağa, Turkey. The filler, expanded perlite, was supplied from Etibank, Cumaovasi Perlite Plant, Turkey. The properties of HDPEs, and the chemical composition and some physical properties of the expanded perlite, are given in Tables I and II, respectively. The silane coupling agent γ-APS, coded A-1100, was supplied by Union Carbide.

Preparation of Perlite and Application of γ-APS

Before the perlite was incorporated into the polymer matrix, it was dried at 100°C in an oven for 24 h and then sieved. The fraction under 400-mesh sieve was collected and used. The average particle size was measured as 5.0 μm by a Shimadzu SA-CP3 analyzer, based on the sedimentation technique.

The silane coupling agent γ-APS was applied to perlite (2% w/w) from ether and water solutions. The former silane application is considered as dry blending. The solvent, ether, was removed at 80°C overnight to complete dryness. In the aqueous application of γ-APS, the hydrolysis of the silane coupling agent is double-distilled water before the treatment with perlite was of concern. Perlite was added into the silane coupling agent containing aqueous solution and the slurry was left at room temperature for one hour. Then water was removed at 100°C overnight where a complete hydrolysis reaction between silanol groups of the silane coupling agent and surface hydroxyls of the perlite was achieved.

Table I   The Properties of HDPEs Used

Type of HDPE	MFI (g/10 min) (2.16 kg)	ρ (g/cm³)	$\overline{Mw} \times 10^{3}$**	$\overline{Mn} \times 10^{-3}$**	H.I.
H02054P	2.00*	0.954	290	32	9.1
F0753	0.70	0.953	207	24	8.6
00660P	0.60	0.960	130	20	6.5
S0464	0.35	0.964	124	19	6.6

* 21.6 kg.

** H02054P and 00660P are the results of producer company; the others were obtained from Gel Permeation Chromatography, Waters 150°C.

Table II **The Chemical Composition and Physical Properties of Expanded Perlite**

Chemical Composition (%)		Physical Properties
SiO_2	71.0–75.0	Color: Grayish white-pearly appearance
Al_2O_3	12.5–18.0	T_S = 870–1100°C
Na_2O	2.9–4.0	T_m = 1260–1340°C
K_2O	4.0–5.0	pH = 6.6–8.8
CaO	0.5–2.0	Specific Gravity = 2.2–2.4
Fe_2O_3	0.5–1.5	Bulk Density = 250–1000 kg/m³
MgO	0.1–1.5	Max. Moisture (from air) = 0.5%
MnO_2	0.03–0.1	Hardness (mohs) = 7.0
TiO_2	0.03–0.1	Surface Area = 1.88 m²/g
Other oxides	0.00–0.01	Shape = Irregular flake

Sample Preparation and Testing

The untreated and treated perlites were mixed with polyethylenes at different weight percentages—10, 15, 20, 25, 30, 40, 50, and 60—in the mixing head (W 30 H) of a Brabender Plasticorder PLV-151. The corresponding volume fractions were calculated on the basis of the densities of pure polyethylenes and perlite. The volume fractions were 0.043, 0.068, 0.094, 0.121, 0.151, 0.217, 0.293, and 0.383, respective to the weight percentages.

The Brabender was operated at 190°C oil bath temperature and the mixing was carried out with a rotating speed of 60 rpm for 10 min to obtain complete dispersion. During mixing, Dilaurylthiopropionate (Plastanox-LTDP), a product of American Cyanamid Co., was used as an antioxidant at the concentration of 0.5% with respect to the polymer weights.

2.0-mm-thick samples from these composites were prepared for tensile tests by compression molding at 200°C and 1400 kg/cm² between steel plates. The temperature was allowed to decrease to 175°C at the same pressure and then the mold was cooled by circulating tap water at room temperature. Although perlite powder had a grayish-white color with a pearly luster, the color of the composites varied from light yellowish-green (10%) to dark khaki (earth-colored) (60%). The color variation did not change greatly with the silane coupling agent application.

Tensile tests were performed in an Instron tensile testing machine (TM 1102) with dumbbell-shaped standard samples at room temperature. The draw rate for the elastic modulus determination was 0.31 cm/min, and for the ultimate properties it was 5.0 cm/min. In both tests, the gauge length was 5.0 cm.

The fractured surfaces of the polyethylene composites were examined by a Cambridge S4-10 Doublescan scanning electron microscope at different magnifications, after protective gold coating.

In addition to these tests, a prior test had been applied to determine the extent of branching in terms of —CH_3 groups in HDPEs by IR spectroscopy (Perkin–Elmer 177) as described elsewhere.[30] F0753 was found to have 15.2 CH_3 groups/1000 carbon atoms, where the other HDPEs used had no measurable —CH_3 groups.

RESULTS AND DISCUSSION

Ultimate Tensile Strength

The variation of ultimate tensile strengths as a function of perlite content of the HDPE-perlite composites are given in Figure 1. The corresponding volume fraction of perlite (Ψ) in the polymer matrix is given above the figure and the other following figures. With the addition of perlite, the ultimate tensile strength increases from approximately 25 MPa to 40 MPa. The difference between silane-treated (for both kinds of treatment) and untreated perlite composites appears to be small but distinguishable within the experimental error. In general, all data points represent the average of at least ten measurements and the standard deviation from the figures' mid data points is around 1 MPa. The hydrolyzed silane-treated perlite shows a little better ultimate tensile strength compared to that given dry silane treatment. However, the variation of silane coupling agent depends on the filler concentration and the type of the polymer.

We observed two exceptions in the increasing trend of the composites' tensile strength: H02054P and F0753. In the former (Fig. 1a), after the initial concentration of perlite, the ultimate tensile strength showed a minimum; this corresponds, whether the filler was treated or untreated, to 20% by weight composition. This minimum could be considered to be a gap in the expected improvement in the ultimate strength. Hence, the lines were interrupted at this region instead of following the data. This reduction can be explained from stress–strain curves. As given in Figures 2(a) and 2(b), 10% perlite-filled H02054P composites drew before they failed and the failure was fibrillar in nature (see also Figure 7), similar to pure H02054P. With the increasing amount of perlite (i.e., 20%), orientation
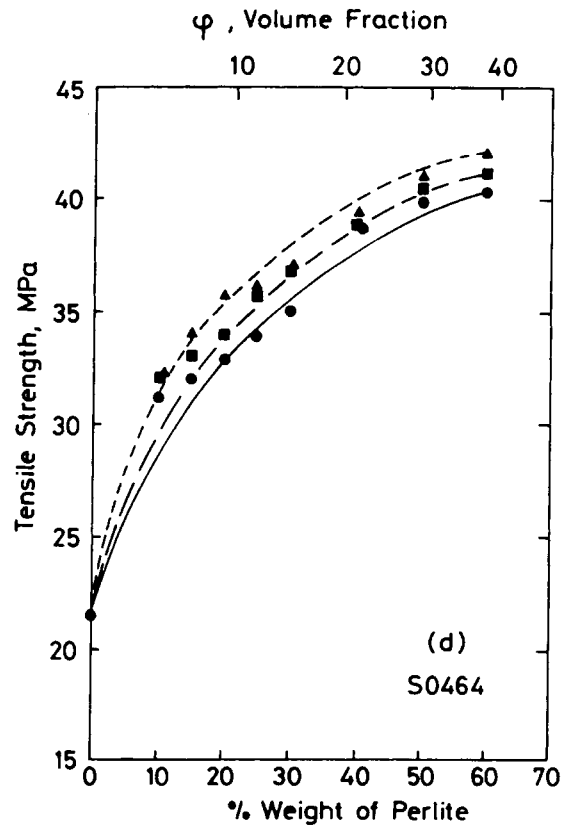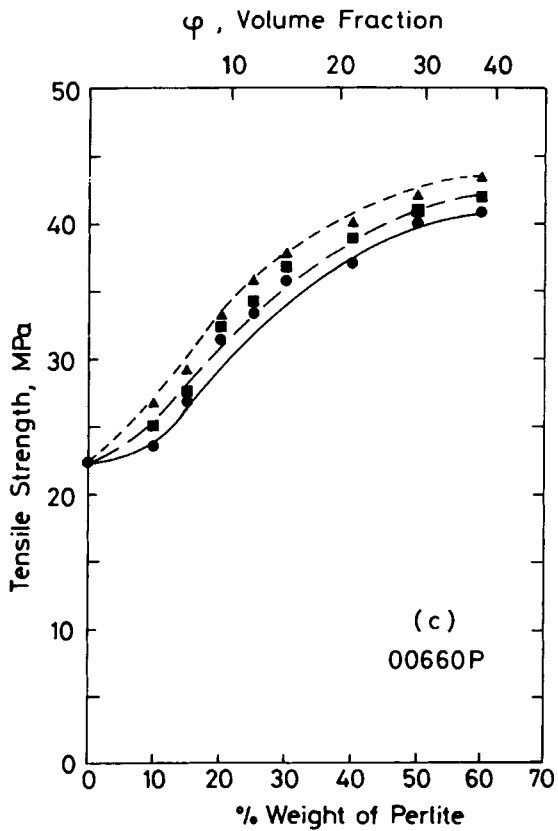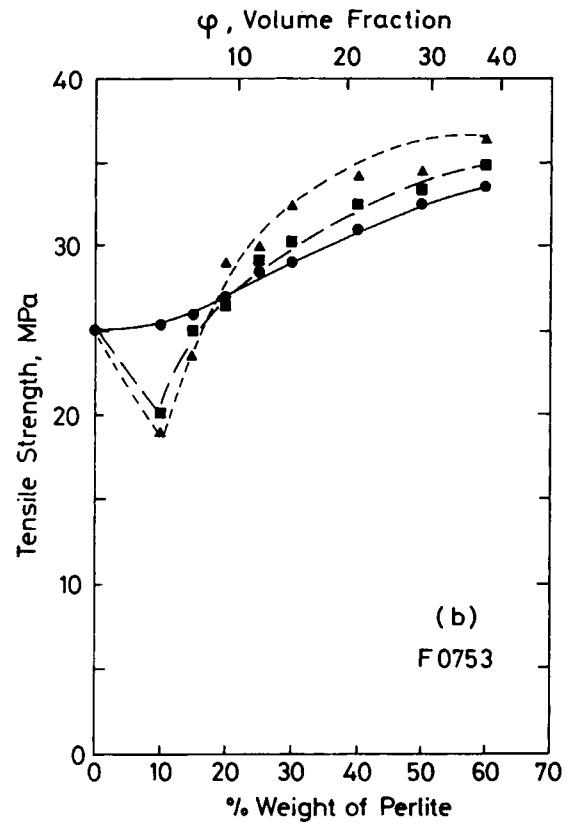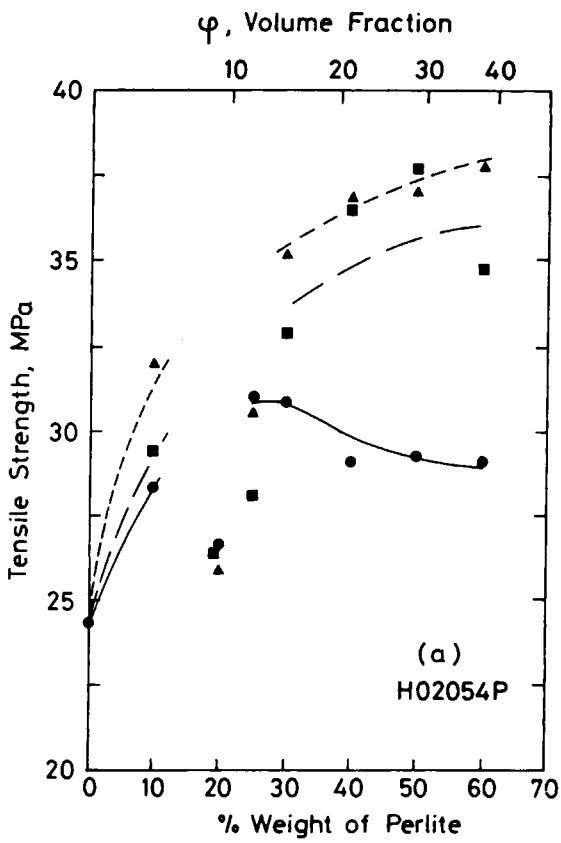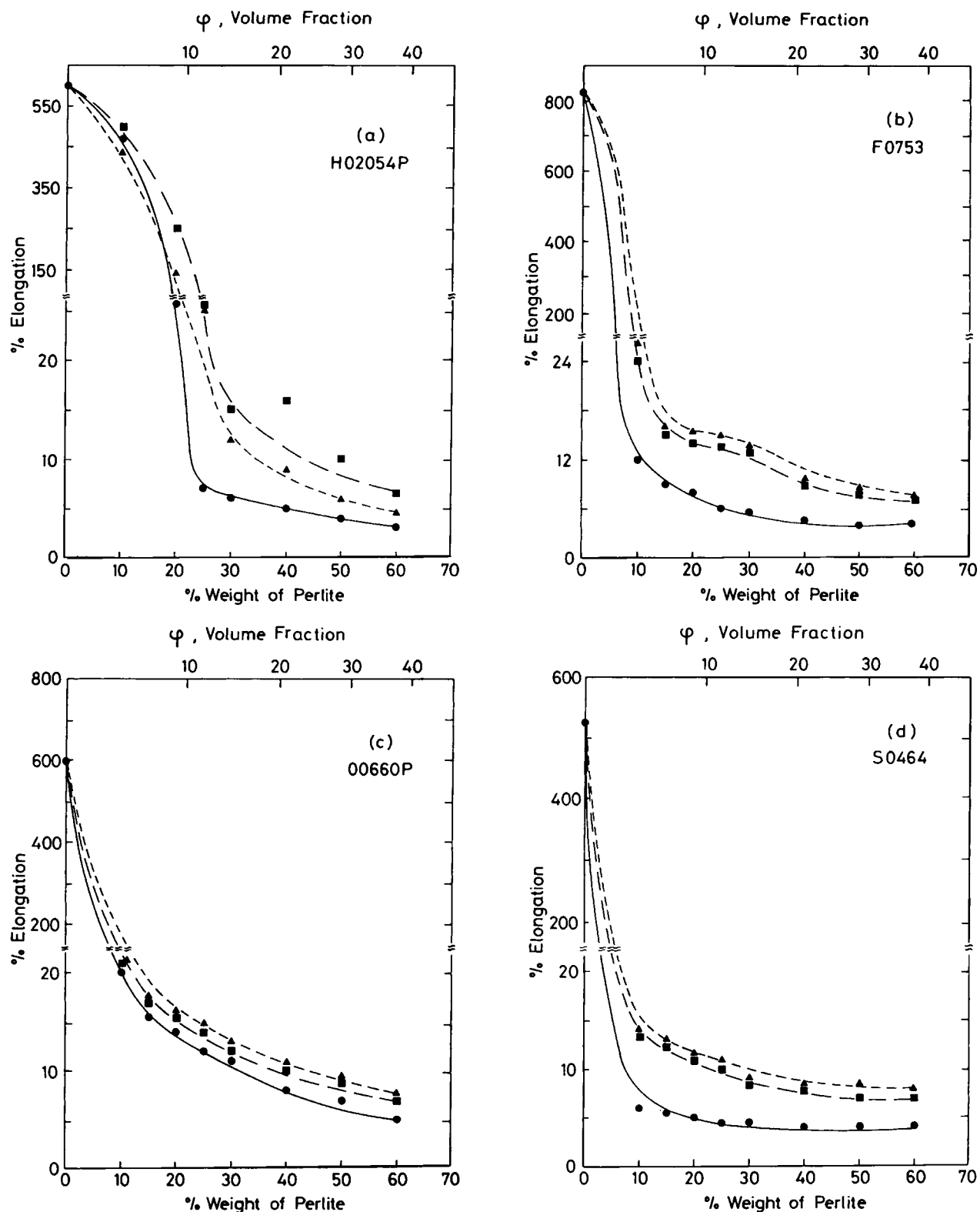
Figure 1 Variations of ultimate tensile strength with concentration of perlite for HDPE composites. (a) H02054P, (b) F0753, (c) 00660P; and (d) S0464. Symbols are used for untreated perlite (●), dry silane treated perlite (■), and hydrolyzed silane treated perlite (▲). The corresponding volume fractions in terms of percentages are given above the figures.
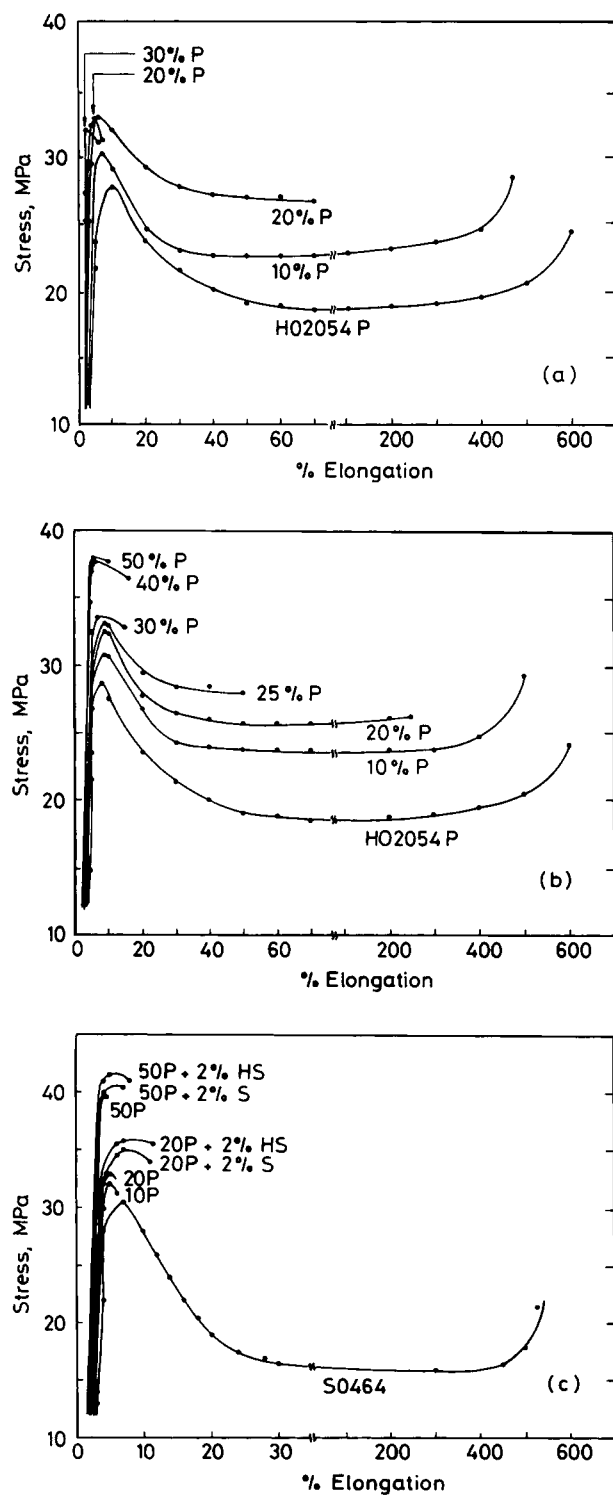
Figure 2 Stress–strain curves of composites at various compositions. (a) untreated perlite filled H02054P, (b) dry silane treated perlite-filled H02054P, and (c) perlite-filled S0464, where P, S, and SH stand for perlite, dry silane treatment of perlite, and hydrolyzed silane treatment of perlite, respectively, and the numbers refer to weight percentages of perlite and silane treatment.

was largely inhibited and the composites broke during the strain hardening period with a smaller ultimate tensile strength compared to the 10% perlite-filled composites; yet the corresponding stress at a given strain was higher than that of 10% composition. In 25% untreated perlite composites, the ultimate tensile strength was found to be higher than that in the 10% and 20% perlite compositions. Upon silane treatment (both hydrolyzed and unhydrolyzed), similar behavior was noted, with additional improvement in elongation [Fig. 2(b)] compared to the untreated 25% composites, which broke just after yielding. The yield stress variation and the yield behavior of these composites have been discussed in a separate paper.[31] Silane coupling agent enabled the composites to have measurable yield stress values at the higher perlite concentrations, for which the untreated perlite composites usually failed before the yield point. Only for polyethylene H02054P did we observe a large difference in the ultimate strength between untreated and silane-treated composites. While the ultimate tensile strength of the untreated perlite composites showed a reduction after the peak at 30% composition [Fig. 1(a)], the silane treatment appeared to cause further improvement in tensile strength. The enhancement in tensile strength upon silane treatment is largely due to the increased adhesion between the filler particles and the high molecular weight, highly viscous H02054P. [Figure 2(c) shows how γ-APS affects the stress-strain properties of S0464 composites.]

In the case of F0753 composites, the ultimate tensile strength increased with increasing perlite content [Figure 1(b)]. Good adhesion exists between perlite and polymer, like the other composites, particularly after the γ-APS treatment. However, there is an unusual decrease in ultimate tensile strength at 10% and 15% with the treated perlite-filled F0753 composites. γ-APS probably acts as a plasticizing agent, which can be supported by the behavior of increasing elongation at break [Fig. 3(b)] while decreasing ultimate tensile strength and elastic modulus [Fig. 4(b)]. The presence of branching in F0753 appears to be another influencing factor. It has been reported that some coupling agents might have a plasticizing effect on the polymer with short branches, rather than the polymer with straight chains, by increasing the compatibility of the filler with the polymer.[2] As mentioned in the Experimental section, the branching for F0753 was found to be 15.2 —CH_3 groups/1000 carbon atoms. On the other hand, there were no measurable branches in the other HDPEs studied. Above 15% perlite, the silane treatment suddenly augments ul-

Figure 3   Variations of elongation at break with perlite concentration for HDPE composites. (a) H02054P, (b) F0753, (c) 00660P, and (d) S0464. Symbols are used for untreated perlite (●), dry silane treated perlite (■), and hydrolyzed silane treated perlite (▲).
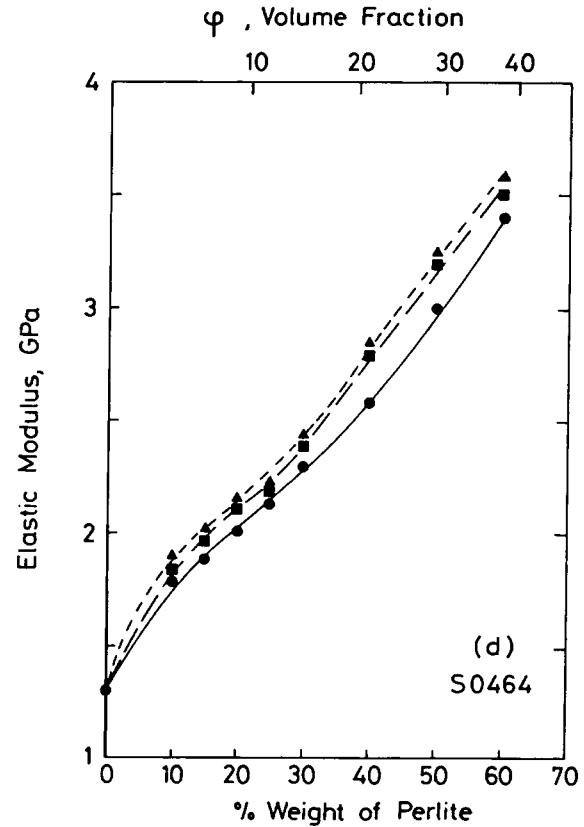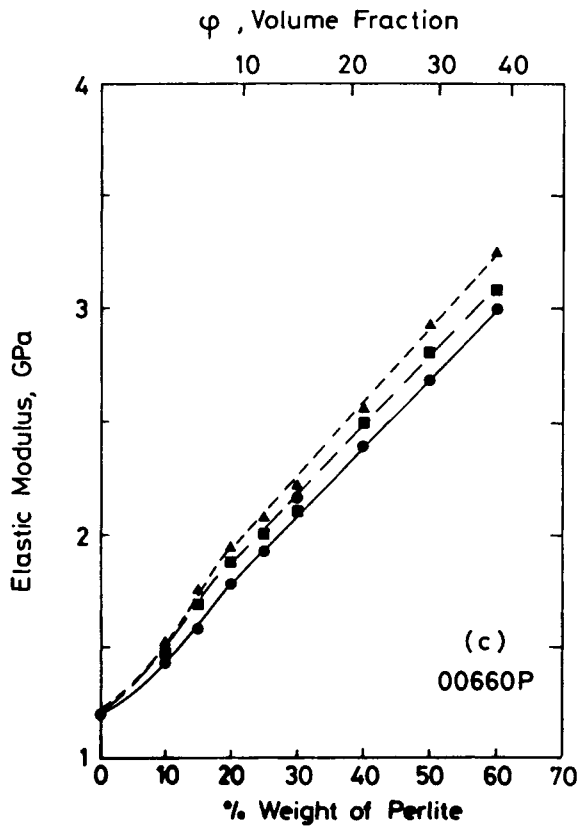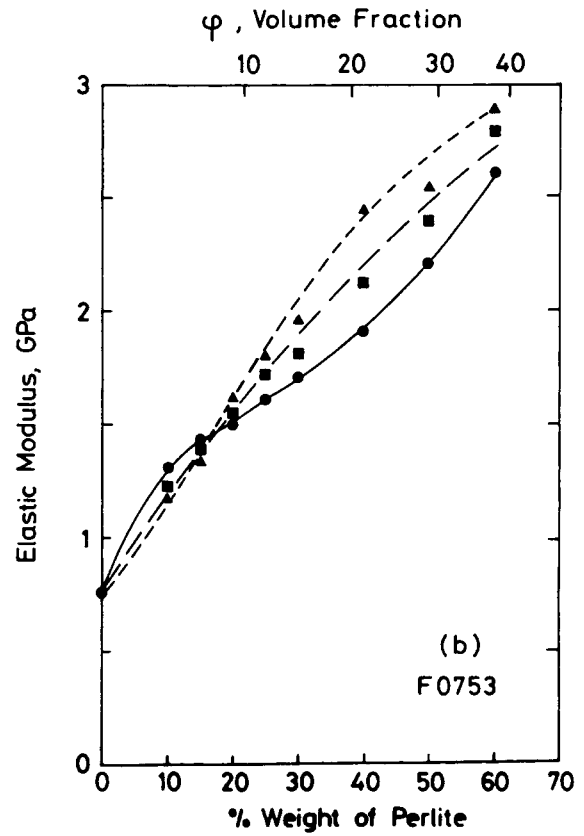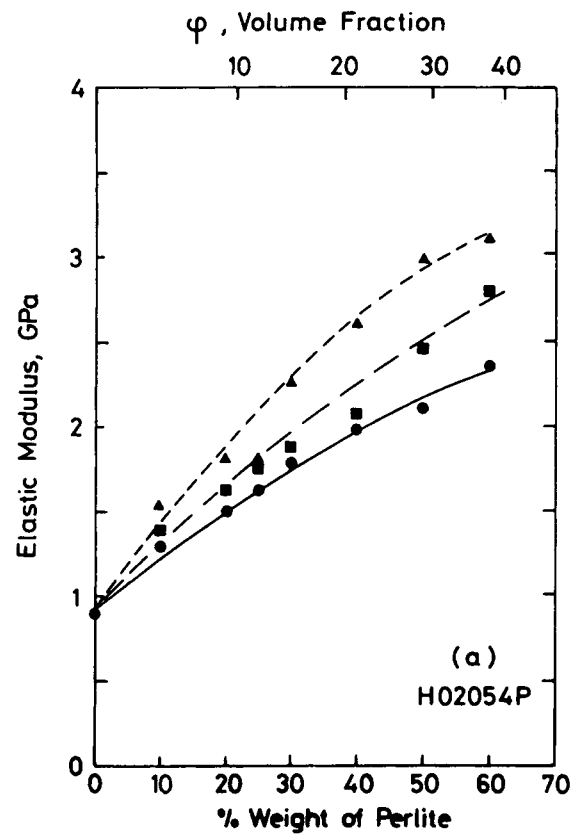
Figure 4 Variation of elastic modulus with perlite concentration for HDPE composites. (a) H02054P, (b) F0753, (c) 00660P, and (d) S0464. Symbols used for perlite treatment are the same as those in Figures 1 and 3.

timate tensile strength, especially after 25%. This improvement seems to be substantially greater for hydrolyzed γ-APS. Treated perlite particles can prevent the flexibilities of short and long chains due to the enhanced adhesion, hence tensile strength at break increases.

In 00660P and S0464 composites [Figures 1(c) and 1(d)], the ultimate tensile strength increased with the amount of perlite, showing the existence of good adhesion between the perlite and polyethylenes. The highest increase among the studied polyethylenes was observed in S0464 polyethylene. This polyethylene shows high crystallinity compared to the others, and the addition of a small amount of perlite makes the composite very strong and rigid by increasing the ultimate tensile strength and decreasing elongation at sudden break. It appears that inherent crystallinity is an effective property in significant improvement in the tensile properties.

The variation in ultimate strength of pure polyethylenes follows the order of S0464 < 00660P < H02054P < F0753, which can be followed from Figure 1. The ultimate tensile strengths of polyolefins are well known to be closely related both to the molecular weight and to the inherent crystallinity. Although pure S0464 and 00660P have the lowest ultimate tensile strength values, the most significant increase in tensile strength at break is observed in their composites upon the addition of perlite. Ultimate tensile strength values of S0464 composites are greater than for the other polyethylenes at all concentrations of perlite, reaching a maximum value of 43 MPa for hydrolyzed silane-treated perlite at 60% composition. S0464 becomes stronger and stiffer by the addition of perlite in which two materials, the crystalline part of PE and perlite, cause this sudden increase in tensile strength, while the amorphous part of polymer is dispersing the stress. Perlite addition results in a monotonic increase in ultimate tensile strength in 00660P composites at the low concentrations of filler, but the ultimate strength approaches the value for S0464 composites at the higher filler content. The untreated perlite addition increases ultimate tensile strengths of H02054P composites more than F0753 composites of up to 25–30% perlite, then the values for H02054 composites decrease because of poor stress transfer. After 30% perlite, ultimate tensile strengths of F0753 are greater than H02054P composites. However, silane-treated perlite H02054P composites are found eventually to have higher strength than F0753. The treatment of perlite with γ-APS did not greatly affect this order in polyethylene composites when compared to untreated perlite, except for the mentioned H02054P–F0753 difference.

Elongation at Break

In pure polyethylenes, F0753 has the highest percent of elongation, nearly 850%, and S0464 has the lowest (about 575%), while elongation at break of 00660P and H02054P are nearly equal. Elongation at break decreases rapidly with the introduction of perlite as shown in Figures 3(a)–3(d) and the stress–strain curves (Fig. 2). This is expected, since more and more experimental strain is absorbed by less polymer. Composites become more brittle with increasing amounts of perlite. As has been well described,[23] the addition of very stiff filler forms stresses concentration points and the samples rapidly fracture when stress is applied. A 10% perlite addition resulted in a sudden fall in elongation for F0753, S0464, and 00660P composites, but was seen after 20%–25% perlite addition for H02054P composites. As mentioned previously, 10% perlite-filled H02054P composites show orientation and fail in a similar way to pure H02054P. Although not conclusive, this may be due to the comparably high molecular weight of H02054P.

The greatest reduction in elongation at break was observed for S0464 composites, obviously due to its inherent properties, i.e., high crystallinity. The high crystallinity accompanied by perlite makes composites even more brittle. The decrease for F0753 is worth mentioning because by the addition of 10% perlite, % elongation reduces to 12%. The decreased flexibility of short chain branching in F0753 by the filler makes the composite more brittle, hence suddenly reducing the ultimate elongation to small values.

Apparently, silane coupling agent improves elongation at break in all composites studied. The most significant improvement in % elongation was seen in F0753 and S0464 composites, nearly a 100% increase compared to the corresponding untreated perlite compositions.

Elastic Modulus

The elastic modulus increases with perlite content in the composites as shown in Figures 4(a)–4(d). The increase in elastic modulus with perlite addition is expected, since flexing of the matrix is prevented by relatively high modulus filler particles. In the case of untreated perlite-filled HDPEs, it was observed that the elastic moduli in H02054P and F0753 were nearly equal. However, S0464, which originally had the highest elastic modulus among the polyethylenes, showed the biggest modulus increase in the composites. The 00660P composites placed between S0464 and the other two, H02054P and F0753. This
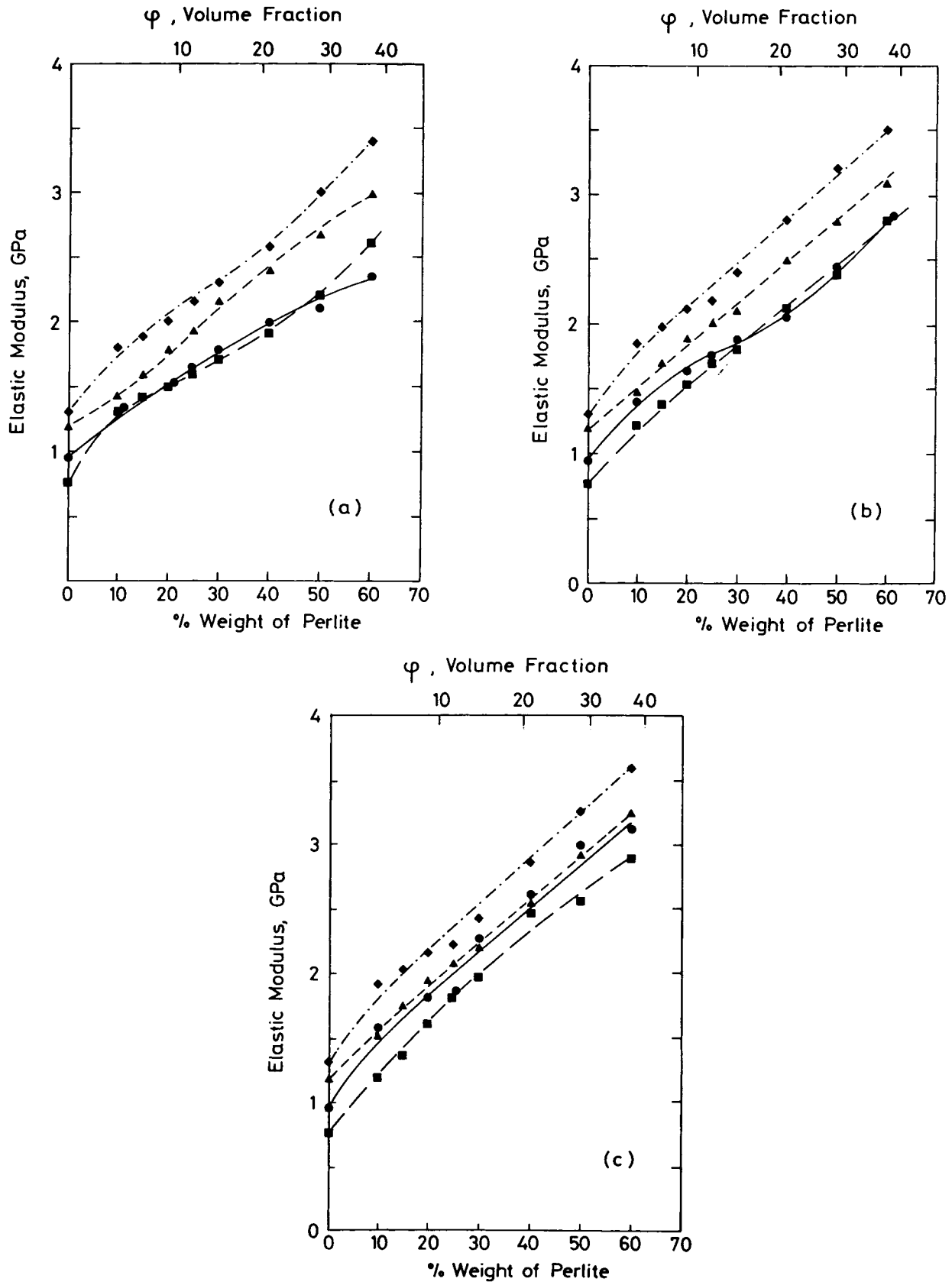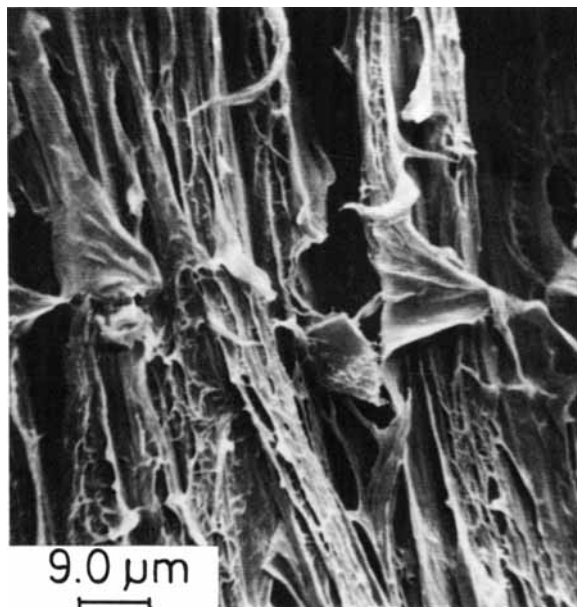
Figure 5 Comparison of elastic modulus of perlite–HDPE composites. (a) Untreated perlite-filled composites, (b) dry silane-treated perlite composites, and (c) hydrolyzed silane-treated perlite composites.

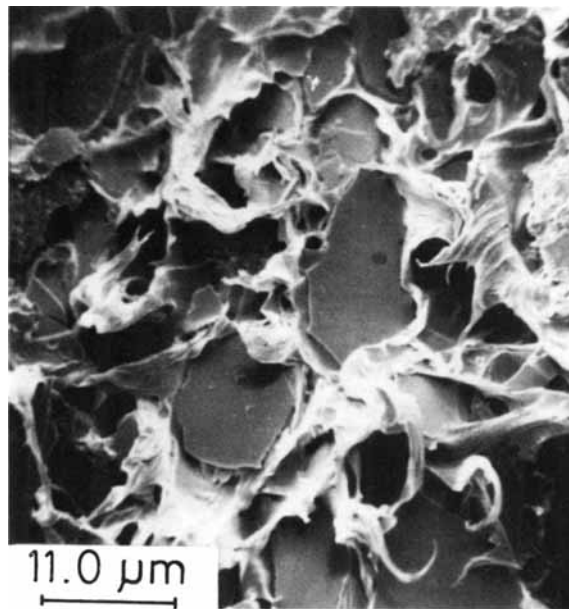comparison is given for all perlite composites in Figure 5.

Silane treatment enhances stiffness in all composites but does not greatly alter the order of elastic modulus values; i.e., again, highly crystalline, low molecular weight polyethylenes show higher elastic moduli. The low elastic modulus in F0753 at 10–15% perlite compositions may be ascribed to the presence of branching in F0753 as discussed previously. Figure 5 clearly indicates the difference between treated and untreated perlite-filled composites, which becomes still more obvious at high loadings of perlite. Such contribution was already ascribed to a decrease in the formation of vacuoles[9] at high concentrations of perlite by the presence of the coupling agent. Hydrolyzed silane-treated samples have higher modulus values than unhydrolyzed ones. Consequently, the interfacial adhesion can be said to be improved by means of the hydrolysis procedure.

Scanning Electron Microscopy Study

Fractured surfaces of the mechanically tested composites were studied by SEM to visualize the existence of adhesion between the filler and the polyethylenes. Through Figures 6–10, our discussion is aimed at showing the interfacial adhesion in these composites, including the behaviour of H02054P at low loading of perlite.
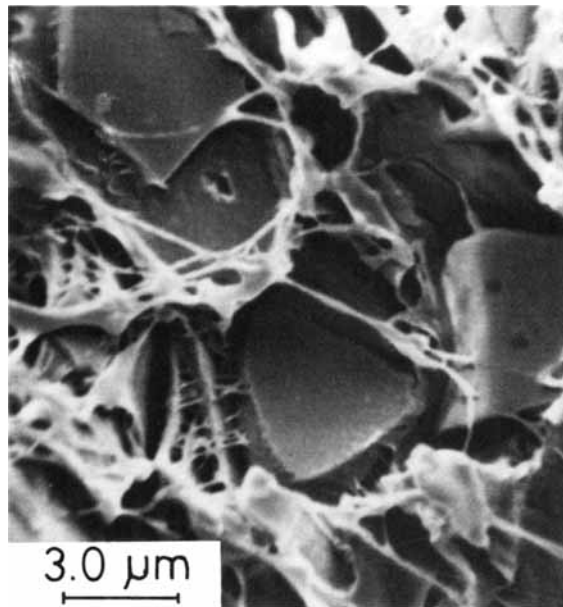

Figure 7 Scanning electron micrograph of 20% untreated perlite–H02054P composite on the tensile fractured surface.
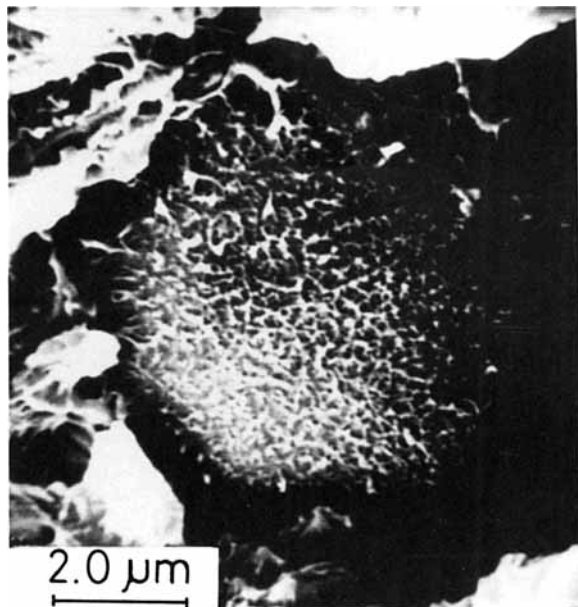
Orientation of polyethylene chains in 10% dry silane-treated, perlite-filled H02054P is apparent in Figure 6. This fractograph shows that the perlite particles are driven out of the polyethylene matrix, while polyethylene shows orientation along the draw

Figure 6 Scanning electron micrograph of 10% untreated perlite–H02054P composite, along the fractured surface of mechanical test.
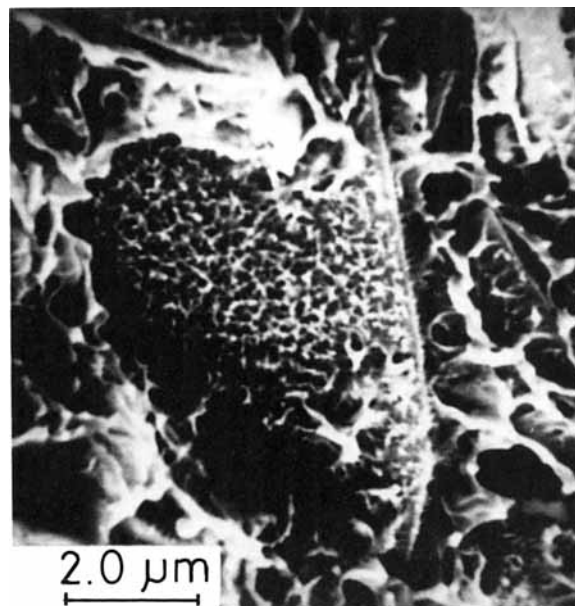

Figure 8 Scanning electron micrograph of 50% dry-silane-treated perlite-H02054P composite, the tensile fractured surface.

direction. Furthermore, perlite particles adhered to the matrix and resulted in splitting the polymer matrix along the draw direction. In the untreated perlite application, however, the perlite surface is apparently very clean, without any remaining indication of adhesion (Fig. 7). Although the surface of perlite particles seems to be clean after dry-silane treatment, through the edges of the perlite particles we observe microdrawing of polyethylene due to strong adhesion between perlite and polymer, as given in Figure 8. This type of interfacial bonding was reported to be direct bonding of polyethylene to the surface through bridging silane molecules in HDPE/azido functional silane/glass composites.[24] In addition, this type of bonding had a small influence on the dynamic–mechanical properties of polyethylenes.[24,25] Moreover, it should be kept in mind that perlite is a volcanic silicate and its chemical composition is quite similar to E-type glass.

The hydrolysis procedure during silane treatment of perlite fillers not only improves the mechanical properties studied but also causes a change in the fracture morphology by increasing the thickness of the bound polyethylene on the filler surface (Figs. 9 and 10). In these micrographs, the presence of a layer of bound polyethylene on the perlite surface is clearly apparent. The migration of monomeric or low molecular weight oligomers of the silane into a region of polyethylene surrounding the filler was

Figure 10   Scanning electron micrograph of 30% hydrolyzed-silane-treated perlite-00660P composite, the tensile fractured surface.

suggested to result in this type of interfacial bonding.[24] The migration of γ-APS into the polyethylene phase was also reported by Sung et al.[32] In our study, the matrix polyethylene left on the filler surface exhibits microdrawing. This behavior suggests that there exists a strong interaction between perlite and polyethylene. These micrographs demonstrate the effective and improved interfacial adhesion between perlite and HDPEs, in particular hydrolyzed γ-APS-treated perlite application. The interaction between perlite and polyethylenes is found to be independent of polyethylene type.

CONCLUSIONS

Ultimate tensile strength and elastic modulus increase with the amount of untreated perlite, while ultimate elongations show a drastic drop compared to virgin polymers, particularly in branched polyethylene F0753 and highly crystalline polyethylene S0464. γ-APS treatment substantially improves ultimate tensile strengths, elastic moduli, and elongations at break. The exceptions of ultimate properties, such as the decrease in ultimate tensile strength after 30% untreated filler in H02054P and the reductions of ultimate tensile strength and elastic modulus at γ-APS-treated filler concentrations of 10% and 15% in F0753, may be attributed to poor

Figure 9   Scanning electron micrograph of 60% hydrolyzed silane perlite–F0753 composite, the tensile fractured surface.

stress transfer between the filler and H02054P and the presence of branches in F0753, respectively. The high inherent crystallinity of S0464, although it has the lowest molecular weight among those examined, seems to be very effective in increasing ultimate tensile strength and elastic modulus. A significant improvement in mechanical properties is observed upon γ-APS application. The hydrolyzed silane treatment appears to be generally more effective than the dry silane treatment.

SEM studies indicate that interfacial adhesion between perlite and HDPEs is improved by using γ-APS, through bridging and migration of monomeric or low oligomeric silane molecules into the polyethylene phase.

Perlite, being an irregular flake-type filler, may be used as a reinforcing agent for semi-crystalline polymers, like the HDPEs studied in this work.

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