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A study on the yield stress of perlite-filled high-density polyethylenes

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Four different types of high-density polyethylenes were blended with expanded perlite at different compositions. γ-aminopropyltriethoxysilane was applied to perlite (2 wt%) from ether and water solutions to enhance the interfacial adhesion between the polymer and the filler. It was shown that silane treatment advances the yield stress with improving dispersion and increasing the interfacial adhesion of the filler with the polymer matrix. The experimental results were then checked with the expression of Turcsanyi *et al.*'s.

1. Introduction

The mechanical properties of filled polymers have been widely investigated in detail and various theoretical approaches have been suggested concerning the shape, size, size distribution and interfacial strength. Among the mechanical properties of filled polymers, the yield stress was, however, less tractable [1–9]. One of the reasons concerning yield stress is the complexity of the load transfer mechanism between the continuous phase and the filler. On the other hand, the yield stress appears to be very crucial since it gives information about the maximum allowable load without considerable plastic deformation. Glass bead–SAN [1], mica–LDPE [2], mica–PP [3], clay–polyester [4], $CaCO_3$–PE [5, 6], kaolin–PE [5] and other systems [7–9] are examples of yield-stress studies of filled polymers. In most of these examples appearing in the literature, the yield stress of the composites showed a decrease with increased filler content, indicating that the load transfer between the polymer and the filler was inhibited during the drawing process. However, depending on treatment with some coupling agents, the yield stress was found to be improved compared to the untreated filler addition.

Nicolais and Narkis [1] proposed a simple model for evaluation of the yield stress of filled polymers where it was assumed that yielding occurred in the minimum cross-section of the continuous phase perpendicular to the applied load:

$$\sigma_{yc} = \sigma_{yp}[1 - (\phi/\phi_m)^{2/3}] \tag{1}$$

where ϕ and ϕ_m are the volume fraction and maximum packing fraction of the filler, respectively. σ_{yc} and σ_{yp} represent the yield stress of the composite and pure polymer. This equation predicts a descending yield stress with increasing of filler content. According to Equation 1 the matrix cross-section is zero at $\phi = \phi_m$. However, the cross-section of the matrix can be zero only at $\phi = 1$. Turcsanyi *et al.* [9] suggested another equation to solve this problem by using a simple hyperbolic function going through the boundary points $\phi = \psi = 0$ and $\phi = \psi = 1$ to describe the change of effective cross section as a function of filler content, $(1 - \psi)$. They then concluded that a linear dependence of σ_{ym} on ϕ existed and this was then described by the exponential function

$$\sigma_{yc} = \frac{1 - \phi}{1 + A\phi}\sigma_{yp}e^{B\phi} \tag{2}$$

where B is a constant parameter within the validity domain of the equation, but is closely related to the interfacial properties and the yield stress of the matrix; $A = \psi^* - \phi^*/(1 - \psi^*)\phi^*$ where ψ^* and ϕ^* are variables that depend on the packing of the fillers. The value of A varies around 2.0 to 2.5.

The significance of the above equation is that it eliminates the descending trend of the previous one, and also enables us to work with anisotropic composites. Turcsanyi *et al.* [9] showed that nearly 25 polymer–filler systems are in good agreement with their equation.

In this study, we tried to assess the variation of the yield stress of perlite-filled high-density polyethylene (HDPE). Four different commercially available polyethylenes were chosen for this purpose with different properties. The filler used in this work was not a common filler for the polymers. Expanded perlite with irregular flake shape and a microhardness of 7.0 Mohs was applied to the polymer in various proportions. To ensure the highest interfacial adhesion between the polymer and the filler perlite, we selected γ-aminopropyltriethoxy silane (γ-APS) as the silane coupling agent which was previously recommended in particular glassy filler treatments (see for example Ishida [10]) because of the chemical resemblance to glass of perlite, which is a natural volcanic silicate. The experimental results were then checked by using the equation of Turcsanyi *et al.* It was found that there is a good fit approximately up to $\phi = 0.20$; above this

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volume fraction of perlite, deviation between experimental and calculated values was observed.

2. Experimental procedure

2.1. Materials

Four types of HDPE with different properties, coded H020-54P and 006-60P (BP Chemicals, UK) and S0464 and F0753 (Turkish Petrochemical Industry (PETKİM), Aliağa, Turkey) were used as received. The filler, expanded perlite, was supplied by ETİBANK, Cumaovasi Perlite Plant, Turkey. The relevant properties of HDPEs, and the chemical composition and some physical properties of expanded perlite are given in Tables I and II, respectively. The extent of branching ($-CH_3$ group determination) in HDPEs was measured by i.r. spectroscopy with a Perkin Elmer type 177 instrument, as described elsewhere [11]. F0753 was found to have 15.2 $-CH_3$ groups per 1000 carbon atoms, while the other HDPEs used had no measurable $-CH_3$ groups.

2.2. Preparation of perlite and application of silane coupling agent

Before the application of the received perlite to the polymer matrix, it was sieved after drying at 100 °C in an oven for 24 h and 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 analyser based on the sedimentation technique. The silane coupling agent was used to enhance the interfacial adhesion between perlite and HDPE. γ-APS supplied by Union Carbide was applied to perlite (2 wt %) from ether and water solutions without any further purification. The former silane application is considered as dry blending and the solvent ether was removed at 80 °C overnight until complete dryness. In the aqueous application of γ-APS, hydrolysis of the silane coupling agent before the treatment with perlite was performed. The water was then removed at 100 °C in an oven to complete the hydrolysis reaction between silanol groups of γ-APS and surface hydroxyls of perlite.

2.3. 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 wt%) in the mixing head (W30H) of a Brabender Plasticorder PLV-151. The corresponding volume fractions were calculated on the basis of the densities of pure polyethylenes and perlite, and on average they were 0.043, 0.068, 0.094, 0.121, 0.151, 0.217, 0.293 and 0.383 respective to the weight percentages.

The oil bath temperature of the Brabender was adjusted to 190 °C and the mixing was carried with a rotating speed of 60 r.p.m. for 10 min to obtain complete dispersion and better adhesion. During the mixing, dilaurylthiodipropionate (Plastanox-LTDP, American Cyanamide Co.) was used as an anti-oxidant with a concentration of 0.5% with respect to the polymers.

Next, 2.0 mm thick samples from these mixtures were prepared for tensile tests by compression-moulding at 200 °C and 1400 kg cm^{-2} between steel plates. The temperature was allowed to decrease to 175 °C at the same pressure and then the mould was cooled by circulating tap water to room temperature.

The yield strength measurements were performed in an Instron tensile testing machine (TM 1102) with dumbbell-shaped standard samples at room temperature with a draw rate of 5.0 cm min^{-1}.

3. Results and discussion

The variations of the relative yield stress with the volume fraction of treated and untreated perlite-filled HDPEs are given in Fig. 1. The yield strengths of the composites show an ascending trend except in the highest molecular weight HDPE, H020-54P. After $\phi = 0.121$ in H020-54P, the decrease in the yield stress indicates weakening of the adhesion between filler and polymer. This decrease may arise from the difficulty in mixing due to the high viscosity of the polymer, resulting in poor dispersion of the filler and lowering of the adhesion. In the case of F0753 (Fig. 1b) and S0464 (Fig. 1d), the yield strength of the untreated perlite composites became unmeasurable at very low concentrations of filler and the samples failed in a brittle manner before they reached the yield point. Although 006-60P HDPE has almost the same characteristics compared with S0464, with a slightly lower density but higher melt flow index, the yield strengths of these samples are measurable to high filler concentrations, i.e. $\phi = 0.29$. The difference in the melt flow indices possibly imparts the better interaction and dispersion of the filler.

The silane coupling agent (SCA) leads strongly to a higher yield stress when compared with the untreated perlite-filled HDPEs. SCA, whether it was applied dry or hydrolysed, made the composites more ductile, in particular F0753 and S0464. A better dispersion and

TABLE I Properties of HDPEs used

Type of HDPE	MFI (g/10 min) (2.16 kg)	ρ (g cm^{-3})	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	H.I.
H020-54P	2.00[a]	0.954	290	32	9.1
F0753	0.70	0.953	207	24	8.6
006-60P	0.60	0.960	130	20	6.5
S0464	0.35	0.964	124	19	6.6

[a] At 21.6 kg load.

TABLE II Properties of perlite

Chemical composition (%)	Physical properties
SiO_2 71.0–75.0	Colour = white to light grey
Al_2O_3 12.5–18.0	T_s = 870–110 °C
Na_2O 2.9–4.0	T_m = 1260–1340 °C
K_2O 4.0–5.0	pH = 6.6–8.0
CaO 0.5–2.0	Specific gravity = 2.2–2.4
Fe_2O_3 0.5–1.5	Bulk density = 25–1000 kg m^{-3}
MgO 0.1–1.5	Max. moisture (from air) = 0.5%
TiO_2 0.03–0.1	Particle size = 5 μm
MnO_2 0.03–0.1	Surface area = 1.88 m^2 g^{-1}
Other oxides 0.00–0.1	Shape = irregular flake

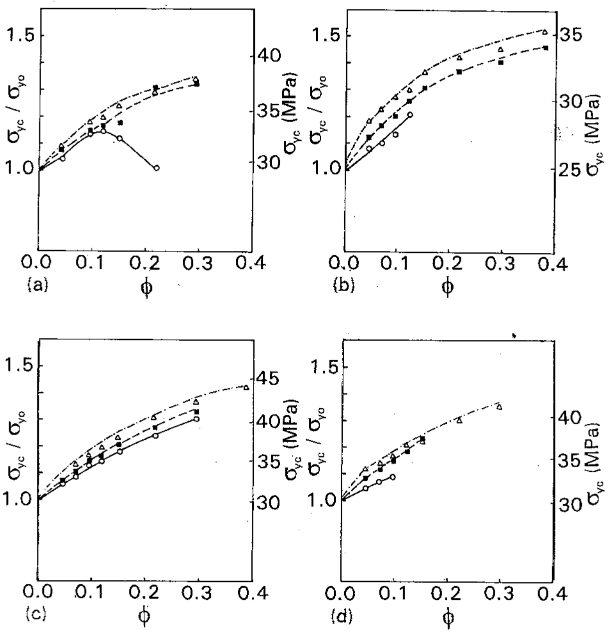

Figure 1 Variation of relative yield stress and yield stress (right-hand scale) with the volume fraction of perlite in HDPE composites for (a) H020-54P, (b) F0753, (c) 006-60P and (d) S0464; (○, ——) untreated perlite, (■, — —) dry silane-treated perlite, (△,—.—) hydrolysed silane-treated perlite.

wetting of the filler were obtained with SCA for H020-54P, where the yield stress showed an increasing trend with the silane-treated filler. When hydrolysed SCA treatment is considered, there is a slight but not negligible improvement compared to dry SCA treatment. Indeed, SCA makes it possible to measure the yield strengths of S0464 and F0753 composites at the higher filler concentrations.

Regarding the influence of the properties of the polyethylenes on the yield stress, although it can be followed from Fig. 1, Fig. 2 was also plotted for the hydrolysed SCA-treated perlite composites. The biggest increase in the relative yield stress is observed in F0753, with σ_{yc}/σ_{y_0} nearly equal to 1.5. However, the relative yield stress changes for the others are almost the same. F0753, as mentioned previously, contains branches while the others do not. SCA and branching appear to play a role in the fast increase in the yield stress. Han *et al.* [12] reported for $CaCO_3$–PP composites that titanate coupling agents had a plasticizing effect on a polymer with short branches rather than a polymer with straight chains, affecting the ultimate strength of the filled polymers. In this case, it is most likely that the plasticizing effect is coupled with the ease of better dispersion and the increased interaction of the filler and the polymer. Another point is that hydrolysed SCA is expected to give silanols [10] which in turn are also expected to react and stick to the surface of perlite particles more strongly than in the dry system. The free ends (propyl groups) of γ-APS then have a higher chance of interacting with the polyethylene, particularly with the branches. Concerning, however, the yield stress values (Fig. 2b), the branched polyethylene (F0753) still exhibits the lowest yield stress. S0464 and 006–60P HDPEs appear to have very close yield stress values and the largest, H020-54P, is placed in between them. Especially if the inherent densities of the polymers are considered, the polyethylenes which possess the higher density (hence correlated with the crystallinity) show the higher yield stress. Although F0753 and H020-54P have the same density, the structural and molecular weight difference results in the apparent variation in the yield stress. The order of pure polymer yield stress values is not disturbed.

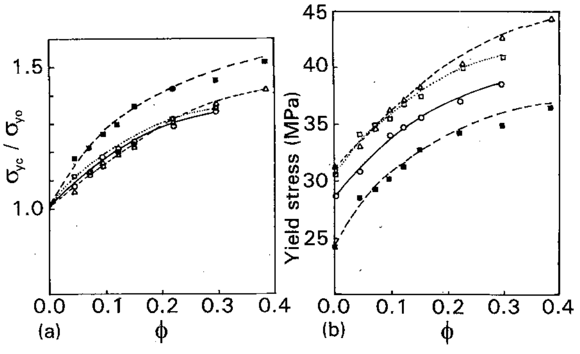

Figure 2 Variations of (a) relative yield stress and (b) experimental yield stress with the volume fraction of hydrolysed silane-treated perlite in HDPE composites: (○, ——) H020-54P, (■, — —) F0753, (△,— — —) 006-60P, (□, . . .) S0464.

The experimental data were then handled using the expression of Turcsanyi *et al.* [9]. Because of its descending nature, the equation of Nicolais and Narkis [1] could not be used. Using Equation 2, the parameters *B* and σ_{y_0} were computed with *A* taken as 2.5. Since *A* is related to packing characteristics of the filler such as shape and size, for an irregularly flake-shaped filler it is rather difficult to establish the correct value of *A*. We therefore tried 2.0 and 3.0 for *A*, but this resulted in larger deviations. For the untreated perlite-filled H020-54P, this calculation is valid for the increasing part of the yield stress. As listed in Table III, *B* values range from 4.937 to 5.355 depending on the yield stress of the pure polymer and the degree of adhesion. *B* values of the SCA-treated perlite-filled polymers are found to be bigger compared to the untreated ones, indicating better incorporation of the filler into the matrix. In F0753, the nearly 6% increase in *B* value is obviously related to the enhanced interfacial adhesion and increased stress transfer between the two components.

A very good linear relation was found in the dependence of σ_{yc} on the filler quantity when

TABLE III Calculated parameters B and extrapolated yield stress of the pure polymer, σ_{yo}, from Equation 2 where $A = 2.5$[a]

	H020-54P			F0753			006-60P			S0464		
	P	PS	PHS	P	PS	PHS	P	PS	PHS	P	PS	PHS
B	5.089	5.161	5.273	4.937	5.133	5.217	5.216	5.233	5.355	5.033	5.255	5.238
σ_{yo} (MPa)	28.32	28.20	27.62	23.87	23.55	24.45	30.06	29.89	29.28	30.52	30.08	30.63

[a] P, PS and PHS stand for untreated, dry silane–treated and hydrolysed silane–treated perlite composites, respectively.

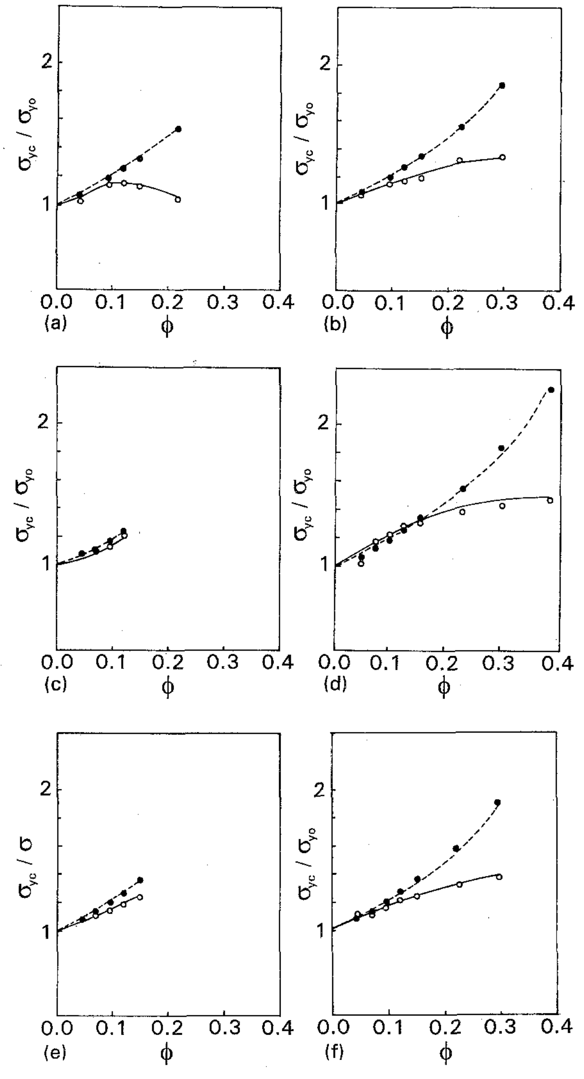

Figure 3 Differences between (○, ——) experimental and (●, — —) calculated relative yield stress values for the selected HDPE–perlite composites: H020-54P, with (a) untreated and (b) dry silane-treated perlite; F0753 with (c) untreated and (d) dry silane-treated perlite; and S0464 with (e) dry silane-treated and (f) hydrolysed silane-treated perlite.

$\sigma_{yc}(1 + 2.5\phi)/(1 - \phi)$ was plotted against ϕ, and B was then calculated. However, when Equation 2 was used for the higher volume fractions, larger than $\phi = 0.2$, it became hard to use. The fit of Equation 2 is good or fairly good below $\phi = 0.2$. Considering the B values derived from the experimental data, the computed yield stress values were plotted for the several composites up to the available experimental yield stress as given in Fig. 3. As can be seen from Fig. 3, the deviation of the computed relative yield stress from the measured relative yield stress becomes larger with the volume fraction.

Apart from geometrical factors, the state of agglomeration of the filler, the variation of the strength of interfacial adhesion and possibly a change in the type of packing with filler content should be taken into account for this difference. The complexity of the load transfer between the polymer and the filler prohibits applying the equation to predict the yield stress at higher filler concentrations for this system. It is well known that irregularly shaped particles, particularly flat ones, provide less support for stress transfer. Therefore, at the higher filler concentrations the experimental values diverge from the predicted values, which points to higher yield stresses.

4. Conclusion

The nature of the polyethylene, its molecular weight, melt flow index and density, and hence the crystallinity and the branching, are the effective factors determining changes in the yield stress. A silane coupling agent not only facilitates dispersion through a plasticizing effect but also improves the adhesion and thus the yield stress. The expression used for theoretical analysis of the yield stress appears to work in the presence of low concentrations of the filler rather than at high concentrations. The deviation between the calculated and measured yield stresses is most possibly due to the increased complexity of interaction of the flaky and irregularly shaped filler with the matrix at high volume fractions.

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