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Mechanical properties of HDPE/magnesium hydroxide composites

S. ULUTAN
Department of Chemical Engineering, Faculty of Engineering, 35100, Ege University, Bornova-Izmir, Turkey

M. GILBERT
Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK
E-mail: M. Gilbert@lboro.ac.uk

Fillers incorporated into polymers for flame retardancy can decrease their mechanical strength. Coating of the filler can enhance the properties of polymer composites. A platy magnesium hydroxide, uncoated, or coated with magnesium stearate or stearic was used as filler in high density polyethylene composites. Tensile and flexural properties were measured. Experimental results were compared with various existing models. Experimental data for both tensile and flexural yield strength showed a good fit to the Pukanszky model. Interfacial interaction was also evaluated through this model. Coating modified tensile and flexural yield strength in different ways. Results were explained by the effect of platelet alignment which was measured by X-ray diffraction. Flexural modulus showed a good fit to the Halpin-Tsai equation, but tensile modulus increased less with filler volume fraction, an effect also believed to relate to filler alignment. Elongation at yield decreased with the addition of filler, more so when coatings were present. This property seemed to be controlled mainly by filler dispersion. *© 2000 Kluwer Academic Publishers*

1. Introduction

Flame retardant and smoke suppressant fillers are becoming of increasing importance, particularly for plastics used in the cable industry, for example. There is a developing interest in magnesium hydroxide as a flame retardant filler that does not produce toxic and corrosive substances during combustion, and can be used at higher processing temperatures than the more widely used aluminium trihydrate [1]. However, fillers can adversely affect some mechanical properties of plastics, and often decrease their tensile strength [2]. The mechanical strength of composites can be enhanced by coating the filler [3]. Coating with fatty acids is widely used, as they are cheap and easy to apply. They also facilitate processing and lower the water adsorption of the composites produced. Recent work has shown that for magnesium hydroxide, stearates, which form ionic rather than stronger covalent bonds with the filler, can have beneficial effects [4, 5].

A number of workers have developed models for the prediction of properties of filled plastics [1, 2, 6–14]. Properties predicted most successfully include modulus, yield strength and elongation at break. The modulus evaluation is easier than that of tensile or yield strength because while the first is a bulk property, the second depends on local polymer-filler interactions [6]. Nielsen [2] stressed that factors affecting the properties of filled systems are often difficult to separate and evaluate in a quantitative manner. The particle size and shape, degree of dispersion, the strength of any aggregates, particle matrix interaction, and the orientation of the particles all affect the mechanical and physical properties of composite materials. As the particle size decreases, the modulus and yield strength increase while the elongation at yield decreases [2]. Composites with geometrically anisotropic particles can behave either as isotropic materils if the orientation of particles is random or as an anisotropic body when the particles are aligned in some manner [7].

Properties of composites containing magnesium hydroxide in polypropylene have been modelled by Jancar [7, 8] and Jancar and Kucera [1], who have studied the effect of filler particle shape and filler matrix adhesion on their yield behaviour and elastic modulus.

The objective of this paper is to investigate the effect that the type of coating on a magnesium hydroxide filler has on the mechanical properties of the resulting composite material. The results are analyzed in terms of the volume fraction of filler using relevant models. Although many equations are found in the literature [2, 6] only those which best fit the experimental data are presented here.

2. Experimental

2.1. Sample preparation

Magnesium hydroxide DP 393, supplied by Premier Periclase (density 2360 kg m^{-3}, surface area 13 m^{2}g^{-1},

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average particle size 0.8 μm [9]) was coated using an 8 litre Fielder High Speed Mixer. Filler and coating agent were heated together for 40 minutes, and reached a final temperature of 120°C. Stearic acid and magnesium stearate (supplied by Fisons) were coated at levels of 6.0 and 6.2% respectively, by weight of filler, to give an experimentally determined monolayer coverage [5, 9, 15].

Varying amounts of coated and uncoated magnesium hydroxide were incorporated into high density polyethylene (HDPE, BP grade HD521 IEA, MFI 11 g/10 min., density 952 kg m^{-3}), using an APV twin screw compounder with a screw diameter of 30 mm, and an L/D ratio of 30 : 1.

The compounds produced were then injection moulded using a Negri Bossi NB55 injection moulder. Tensile bars were produced with a four part mould and used for both tensile and flexural testing.

2.2. Testing

All the species and composites were ashed at 800 °C in an oven in order to calculate the exact amounts of filler incorporated into the HDPE.

X-ray diffraction patterns of magnesium hydroxide powder and the HDPE composites were obtained in the reflection mode using a Hilton Brooks X-ray generator with a Phillips goniometer, operated at 30 mA and 40 kV to produce Ni filtered Cu K_α radiation. X-ray traces were recorded from 2–50°2θ.

Tensile properties were determined according to ASTM-D638-96, using a Lloyd tensile test machine fitted with a 2.5 kN load cell and a cross-head speed of 5 mm per minute. Flexural tests were carried out according to BS 2782 Part-3 Method 335A, using the same instrument, in a three point bending mode with a 50 mm span. Modulus and flexural stress were obtained.

2.3. Models Used

The Pukanszky model [10] relates yield stress to filler concentration, as shown in Equation 1.

$$\sigma_{yc}/\sigma_{ym} = [(1 - V_f)/(1 + AV_f)]\exp(B_\sigma V_f) \qquad (1)$$

where σ_{yc} and σ_{ym} are the yield strengths of the composite and unfilled polymer (matrix), V_f is the volume fraction of the filler, and A is a constant related to filler packing. The first term relates to decrease in effective load bearing cross section, while the second relates to interfacial interaction between filler and matrix. Interfacial interaction depends on the area of the interface, and the strength of the interaction as shown by the following expression.

$$B_\sigma = (1 + A_f\rho_f t)\ln(\sigma_{yi}/\sigma_{ym}) \qquad (2)$$

where A_f is the specific surface area of the filler, ρ_f is its density, and t is the thickness of the interface. From the B_σ values, strength of interaction, σ_{yi} was calculated.

The relative modulus value for a composite containing flakes or platelets that are aligned in parallel with the stress direction is given by Halpin-Tsai equation as discussed by Radosta [11].

$$E_c/E_m = (1 + \zeta\eta V_f)/(1 - \eta V_f) \qquad (3)$$

where E_c is the modulus of the composite and E_m is the modulus of the unfilled polymer. ζ is a geometrical factor which takes into account the filler aspect ratio. η is given by Equation 4:

$$\eta = (E_f/E_m - 1)/(E_f/E_m + \zeta) \qquad (4)$$

where E_f is the modulus of the filler. Radosta suggested that this equation is versatile enough to be used also for flexural modulus [11], as he found the relative values of moduli to be equivalent for flexural and tensile tests.

In order to account for deviations from perfect parallel alignment of filler platelets, Radosta introduced a further parameter, K, into Equation 3, i.e.:

$$E_c/E_m = (1 + \zeta\eta V_f)/K(1 - \eta V_f) \qquad (5)$$

According to Radosta, K varies from 1 for perfect parallel alignment to 3 for a completely random arrangement of the filler.

Application of the Nielsen modification of the Kerner model, Equation 6, which takes into account the maximum packing fraction of the filler particles was also investigated:

$$E_c/E_m = (1 + ABV_f)/(1 - B\psi V_f) \qquad (6)$$

where

$$\psi = 1 + V_f\left[(1 - \phi_{max})/\phi_{max}^2\right] \qquad (7)$$

and ϕ_{max} represents the maximum volume fraction of filler.

$$B = (E_f/E_m - 1)/(E_f/E_m + A') \qquad (8)$$

and A' is a function of the geometry of the particles.

Nielsen also proposed a simple model for the elongation at break for filled composites [12]. In the case of perfect adhesion between filler and polymer, it was shown that,

$$\varepsilon_c/\varepsilon_m = \left(1 - V_f^{1/3}\right) \qquad (9)$$

where ε_c is the elongation of break of the composite, and ε_m that of the matrix.

In the case of no adhesion between filler and matrix, Nielsen calculated the elongation at break ratio from the predicted relative tensile strength, and Equation 11 for modulus ratio for filled systems with no adhesion proposed by Sato and Furukawa [13]:

$$\sigma_{bc}/\sigma_{bm} \approx \left(1 - V_f^{2/3}\right)S \qquad (10)$$

where σ_{bc} and σ_{bm} are tensile strengths of the composite and matrix respectively, and S is a stress concentration function.

$$E_c/E_m = \{1 + [y^2/2(1 - y)]\}(1 - \psi\zeta) - [y^2\psi\zeta/(1 - y)y^3] \qquad (11)$$

TABLE I Properties of magnesium hydroxide/polyethylene composites

Filler	Volume fraction V_f	Modulus E_c MPa	Standard deviation +/− MPa	Yield strength σ_c MPa	Standard deviation +/− MPa	Elongation at break ε %	Standard deviation +/− %
(a) Tensile properties							
	0	308	7.6	18.9	0.44	13.7	0.31
UC	0.048	325	12.8	18.7	0.16	12.1	0.27
UC	0.078	384	25.8	19.8	0.48	10.7	0.71
UC	0.091	386	21.4	19.9	0.43	10.8	0.53
UC	0.147	439	15.8	20.8	0.31	9.0	0.69
MS	0.052	377	30.4	19.0	0.50	10.9	1.01
MS	0.118	397	20.8	17.9	0.20	9.3	0.91
MS	0.125	404	13.7	17.8	0.31	8.5	0.20
MS	0.158	433	9.6	17.5	0.11	7.6	0.28
SA	0.071	356	8.4	18.9	0.27	11.2	0.45
SA	0.122	371	17.0	18.1	0.10	9.5	0.30
SA	0.137	397	19.0	17.9	0.26	8.3	0.26
SA	0.181	412	20.5	17.6	0.32	7.8	0.27
(b) Flexural properties							
	0	762	56.8	24.1	1.02		
UC	0.048	908	106.9	24.3	1.28		
UC	0.078	938	31.7	24.0	0.39		
UC	0.091	1032	19.2	25.9	0.49		
UC	0.147	1116	35.9	27.0	1.10		
MS	0.052	858	0.0	24.9	0.0		
MS	0.118	1313	37.4	27.4	0.18		
MS	0.125	1282	98.7	27.8	0.20		
SA	0.071	947	98.5	26.6	0.65		
SA	0.122	1175	50.4	27.8	0.41		
SA	0.137	1408	86.6	28.3	0.59		
SA	0.181	1696	81.0	30.5	1.23		

UC - uncoated filler; MS - magnesium stearate coated; SA - stearic acid coated.

where $V_f = y^3$, ζ is an adhesion parameter, which is equal to zero for perfect adhesion, and 1 for no adhesion, and

$$\psi = (y^3/3)(1 + y - y^2)/(1 - y + y^2) \qquad (12)$$

3. Results and discussion

Flexural and tensile data for polyethylene composites containing uncoated (UC), stearic acid coated (SA) and magnesium stearate coated (MS) magnesium hydroxide are summarised in Table I. These, together with values calculated from Equation 1 are plotted versus volume fraction in Figs 1 and 2. An upper limit value of $A = 2.5$ was used as proposed by Turcsanyi *et al.* [14] and using a conventional computer fitting procedure, B_σ values and interface yield strengths σ_{yi} given in Table II were found to give a good fit to Equation 1. Matrix yield stress values of 24.1 and 18.9 MPa were obtained from flexural and tensile tests respectively. (The value of t in Equation 2 was taken as 13 nm, previously estimated by X-ray photoelectron spectroscopy [9].)

A number of observations can be made from these results. B_σ values were of the same order as those obtained by Jancar and Kucera for magnesium hydroxide in polypropylene [1], and Raymond for magnesium hydroxide in a higher molar mass medium density polyethylene [9]. The interface yield strengths are much greater than that of the matrix, and are similar to those observed by Raymond, but much higher than those observed by Jancar. It has been suggested [9] that these high yield strengths relate to immobilised polymer around the filler particle, rather

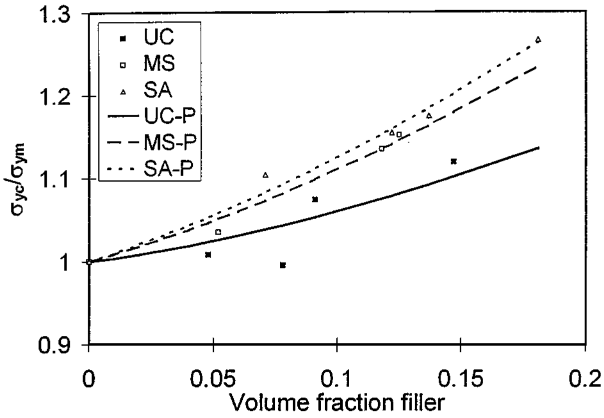

Figure 1 Effect of volume fraction of filler on flexural yield stress. (UC, uncoated, MS, magnesium stearate coated, SA, steraric acid coated. P indicates theoretical values obtained using the Pukanszky model.).

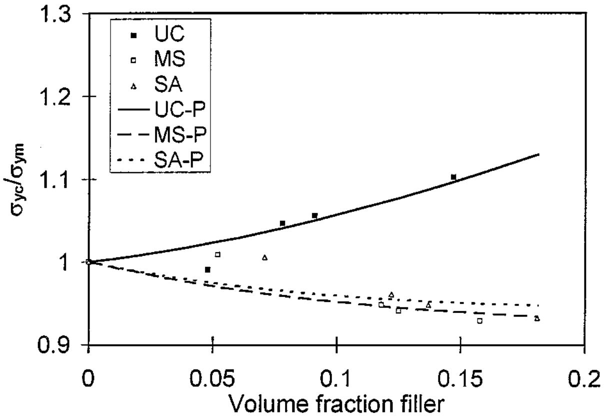

Figure 2 Effect of volume fraction of filler on tensile yield stress. (Captions as in Fig. 1).

TABLE II Composite-filler interface strength parameters

Filler type	Flexural testing		Tensile testing	
	B_σ	σ_{yi} MPa	B_σ	σ_{yi} MPa
UC	3.87	966	3.84	758
MS	4.33	1550	2.79	276
SA	4.46	1757	2.87	298

than to the very thin coating itself. Both flexural and tensile yield strength are modified by filler coating, but in a different way indicating that the behaviour is different under flexural and tensile forces. Results using stearic acid or magnesium stearate as coating are not significantly different.

Tensile yield strength was increased by the introduction of uncoated filler, but coating of the magnesium hydroxide resulted in reduced tensile yield strength (Fig. 1). Similar behaviour was observed by Jancar and Kucera [1] for magnesium hydroxide/polypropylene composites with a filler content less than 0.25 volume fraction. They related this phenomenon to the immobilization of the matrix which was lowered by the surface treatment. In the current study, it was found that the behaviour reversed for the flexural yield strength (Fig. 2). Addition of uncoated and coated magnesium hydroxide increased flexural yield strength, but the effect was greater with coated filler. Also, the interface yield strengths were relatively much higher with the coated fillers present.

The possibility of differences in the effect of filler alignment was therefore considered. Magnesium hydroxide is a platy filler, with a hexagonal unit cell. Filler alignment can be produced by flow along the tensile bars during injection moulding. Alignment of magnesium hydroxide in the mouldings was investigated by X-ray diffraction. Relative intensities of the peaks due to the crystallographic (001) and (101) planes of magnesium hydroxide were measured. The higher the (001)/(101) ratio (R1) the more aligned are the platelets. Alignment of HDPE was also investigated by evaluating the relative intensities of peaks due to (200) and (110) planes (R2 in Table III). As seen in Table III, coated fillers were more aligned than uncoated, and there was also some evidence for increased alignment of polyethylene crystallites, corresponding to more polyethylene chains lying in the plane of the tensile specimen. (It should be mentioned that X-ray diffraction measurements were made on the surface of the tensile bars, so do not reflect the situation throughout its thickness.) Nevertheless, the differences, particularly with respect to filler alignment, could account for observed differences in flexural and tensile testing. When force is applied in a bending mode, it is reasonable to expect that yield strength could be increased by filler alignment. Enhanced filler alignment for coated fillers would then result in a further increase, although the effect of different coatings is not distinguished. During bending, overlapping filler platelets on the contact surface of the specimen would experience compression. The more the alignment, the more the enhancement expected. However, such an effect would not be observed under tension because the filler particles would slip past each other in a vertical direction as the specimen extended. This is reflected in the much lower values of interface yield strength obtained in tension (Table II).

TABLE III X-Ray diffraction data for magnesium hydroxide and composites

Sample	V_f	R1	R2
Magnesium hydroxide	1.0	0.9	—
UC/PE composite	0.09	10.3	0.12
MS/PE composite	0.12	31.0	0.26
SA/PE composite	0.12	23.7	0.26

Attempts were also made to fit moduli data to theoretical models. Data were plotted against volume fraction, together with theoretical values obtained using the Halpin-Tsai model, (Equation 3) in Figs 3 and 4. ζ in Equation 4 is a geometrical factor which takes account the filler aspect ratio. Its value is twice the filler aspect ratio, which was taken as 2 in th present study [9]. It is seen that, within experimental error, there is no significant difference between moduli for coated and uncoated filler for the range of filler volume fractions investigated here. A better fit between experimental and theoretical data was obtained for the flexural test results. Radosta [11] used the modifed Halpin-Tsai equation, introducing an additional factor to account for differing

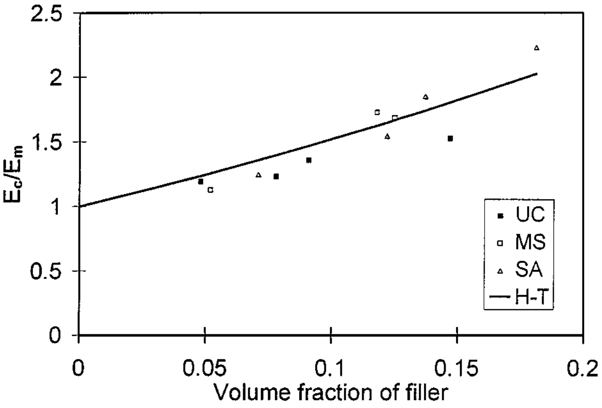

Figure 3 Effect of volume fraction of filler on flexural modulus. (UC, uncoated, MS, magnesium stearate coated, SA, stearic acid coated. H-T indicates theoretical curve obtained using the Halpin Tsai model.).

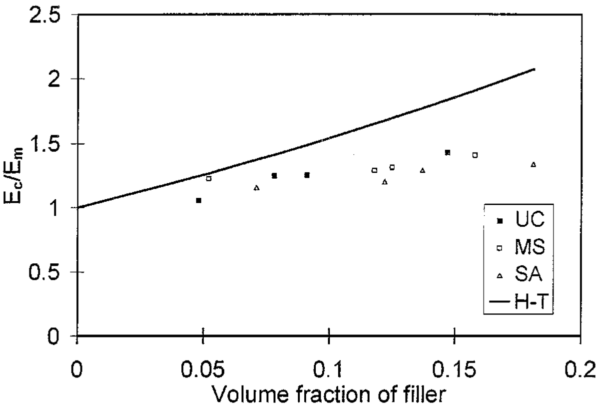

Figure 4 Effect of volume fraction of filler on tensile modulus. (Captions as in Fig. 3).

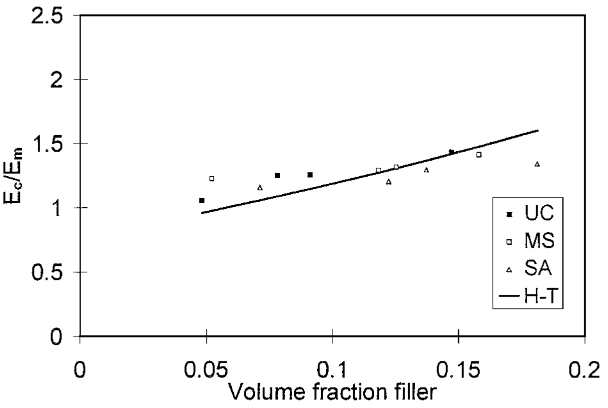

Figure 5 Effect of volume fraction of filler on tensile modulus. (Captions as in Fig. 3). H-T model modified according to Radosta ($K = 1.3$).

filler alignment. Taking the K value as 0.9 and 1.3 respectively for coated and uncoated magnesium hydroxide, Raymond [9] predicted lower moduli for uncoated filler composites. Moduli data from tensile tests are replotted in Fig. 5, together with theoretical data using a K value (see Equation 5) of 1.3, and a better fit is obtained. However, this approach has its limitations; K cannot be constant as E_c/E_m must be equal to one in the absence of filler, and the effect of filler alignment must be a function of the amount of filler present. Clearly, filler alignment is not different in the two types of test, since the same specimens are used.

However, these results suggest that there is a difference, with alignment apparently being poorer when tensile testing is used. In other words, modulus enhancement in flexure was found to be much greater than in tension, whereas similar enhancement of properties was observed by Radosta, but at rather higher filler levels [11]. It can be tentatively suggested that filler alignment is more significant in bending, when the sample surface experiences compression. More detailed X-ray diffraction experiments [16] have shown that filler orientation varies through the thickness of tensile specimens. Under tension, average alignment is important. However, in flexural tests it is possible that surface orientaion has a bigger effect. Jancar [7] also noted the effects of different geometrical modes of loading, and the lack of a theory to successfully take account of this.

Theoretical curves were also obtained using the Kerner equation modified by Nielsen. $\phi_{\max}$ values of 0.345 and 0.530, calculated from oil absorption values of the uncoated and coated magnesium hydroxide respectively [9] were used in Equation 7. The modulus of the magnesium hydroxide was taken to be 64 GPa, as proposed by Jancar [7]. Comparison of Equations 4 and 8 show that B is equal to η if A' is equal to ζ. A' was therefore put equal to 4. Flexural results are shown in Fig. 6. (As before, because of the similarity of Equations 3 and 6, the fit for the tensile data was much poorer, with tensile moduli being less strongly dependent on filler volume fraction.) Because $\phi_{\max}$ values differ for the coated and uncoated fillers, Equation 6 predicts lower moduli for the coated filler composites. However, in practice, there is no significant difference between measured values, and values of modulus do not increase with V_f as much as predicted. The inclusion of the additional term ψ in the Nielsen modified Kerner equation (compare Equations 3 and 6) does not improve the fit between theory and experiment, suggesting a better fit when $\psi = 1$. Jancar [8] has interpreted this situation as complete immobilization of the matrix on the filler, but this seems unlikely at the filler volume fractions used here.

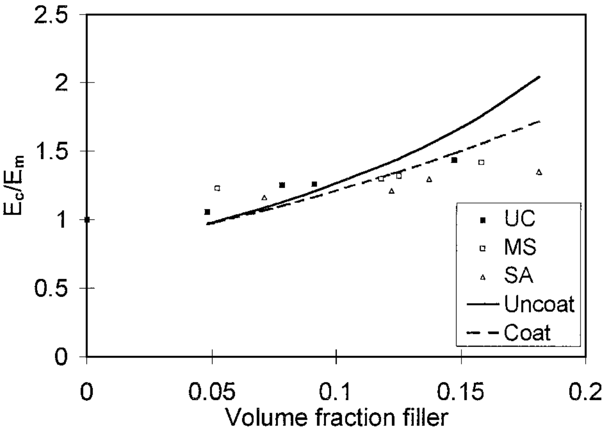

Figure 6 Effect of volume fraction of filler on flexural modulus. (Captions as in the Fig. 3 with the Nielsen modified Kerner model used for coated and uncoated fillers).

The ratio of elongation at yield for the composite and polymer measured in tension is plotted against volume fraction of filler for no adhesion and perfect adhesion, according to Nielsen [12], together with experimental data, in Fig. 7. Elongation at yield was observed to decrease as the volume fraction of filler increased. Values in the presence of coated fillers were lower, and comparison with theoretical plots suggested that coating improved adhesion between filler and matrix. However, this is not consistent either with data in Table II, or with heats of immersion as measured by calorimetry, which suggest that coating decreases filler polymer interaction [9]. Dispersion is improved, and agglomerates broken down, effectively reducing particle size. This will increase surface area, apparently leading to improved interaction at a given volume fraction of filler, and reduced elongation at break [2].

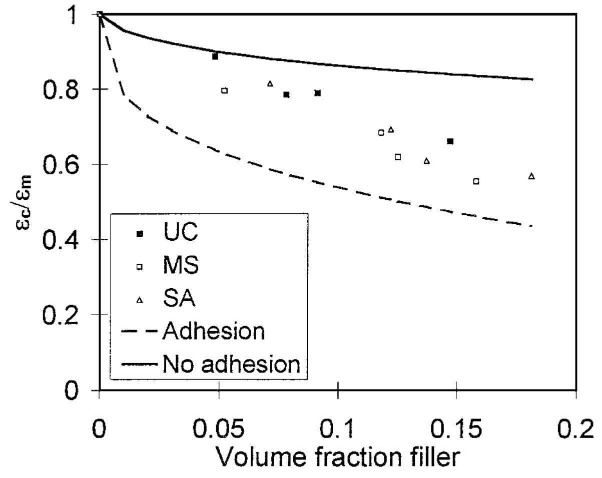

Figure 7 Effect of volume fraction of filler on elongation at (Captions as in Fig. 1). Lines were obtained using the Nielsen model with perfect or no adhesion.

4. Conclusions

Properties of filled compounds are affected by a variety of features including filler coating, filler orientation if the filler is anisotropic, and filler particle size. The effects of filler can be different under different types of loading. Yield strength was increased by the addition of uncoated magnesium hydroxide filler to polyethylene; when the filler was coated with either magnesium stearate, or stearic acid, yield strength in bending increased further, but under tension, it was found to decrease. It was found that coating increased filler alignment, and the effect of this was more significant under flexure. Surprisingly, with the levels of filler used here, this increase in alignment did not affect modulus, with similar results being observed with or without coating. However, again testing mode affected results. Modulus enhancement was higher in flexure than in tension, and use of the Halpin Tsai model suggested that filler alignment had a greater effect in the former case. Elongation at yield decreased with the addition of filler, more so when coatings were present. This was attributed to improved filler dispersion in the presence of coatings.

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