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D. G. Hawthorne[a]; D. H. Solomon[a]
[a] Division of Applied Chemistry, CSIRO, Melbourne, Victoria, Australia

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Reinforcement of Polyethylene by Surface-Modified Kaolins

D. G. HAWTHORNE and D. H. SOLOMON

Division of Applied Chemistry
CSIRO
Melbourne, Victoria, Australia

ABSTRACT

The tensile and impact strength of kaolin-filled polyethylene was found to be dependant on the modulus of the matrix in the vicinity of the filler surfaces and the strength of the filler-matrix bonds, as well as on the degree of dispersion of the kaolin particles on the polyethylene. Improved reinforcement was obtained by the use of novel fillers consisting of kaolin particles encapsulated with high-modulus, surface-bonded, reactive oxyaluminum acylate polymers.

INTRODUCTION

Reinforcement by active fillers is commonly used to improve the mechanical properties of resins, the best known application being the reinforcement of elastomers by carbon blacks. "Inert" particulate fillers, such as kaolin, talc, or whiting, can also greatly improve the tensile strengths and elastic moduli of elastomeric resins.

However, the reinforcing effects of these fillers in glassy or semicrystalline thermoplastic resins is usually limited to modest increases in the tensile strengths of the composites, but with considerable reduction in their impact strengths. Other factors, such as reduced cost, increased stiffness, and abrasion resistance of the composites, are often of greater commercial significance than the increased brittleness of these filled thermoplastics.

The reinforcing effect of inert fillers can be improved by suitable surface treatment of the filler particles to promote wetting by, and adhesion to, the polymer matrix. The reinforcement can be further enhanced if the treated fillers are used in conjunction with additives or treatment which can induce grafting of the matrix to the filler surface during processing of the composites.

A novel technique [1, 2] developed by the Amicon Corporation for the reinforcement of thermoplastics uses specially treated fillers such as kaolin or colloidal asbestos, the particles of which have each been encapsulated with a layer of a relatively high modulus polymer which can bond the matrix to the mineral surface, and which is claimed to act as a graded seal, reducing the formation of deleterious stress concentrations at the matrix-filler interfaces. These modified fillers, known commercially as Ceraplasts, are claimed to yield tough, strongly reinforced composites with polyethylene, although their acceptability is limited by the relatively high cost of the monomers and initiators used in their preparation.

Our aim was to develop more acceptable alternatives to these polymer-encapsulated fillers. We have reexamined the requirements for an effective encapsulating layer and have used the observations reported in this paper to develop several novel methods for the improvement of mineral-filled thermoplastics. One particular method, which employs the surface treatment of minerals with aluminum acylates, is reported in this paper.

EXPERIMENTAL

Materials

Beneficiated kaolins Hydrite-10 and Hydrite 10-S, a predispersed form of Hydrite 10, were supplied by the Georgia Kaolin Co. High-density polyethylene, Hostalen GVP 4760 supplied by Hoechst Australia Ltd., was used as the test matrix. Other materials were normal commercial products or were synthesized by conventional procedures.

Treatment of Kaolin

Kaolins were dried prior to use by heating at 110 to 130° C for at least 4 hr in an air oven. The dry kaolins were then stored in sealed containers.

Reactive Silanes

These were applied by addition of the reagents to vigorously stirred suspensions of the kaolin (30% w/v) in dry hexane at room temperature, the treated kaolins being recovered after 30 to 60 min reaction time by filtration or rotary-evaporation of the resultant dispersions.

Peroxide-Initiated Polymer Encapsulations

Kaolin samples were dry-blended at room temperature with mixtures of monomers and peroxides, the proportions of which, relative to the weight of the particular kaolin sample, are given in Table 1. The blended mixtures were placed in containers which were then briefly purged with nitrogen, sealed, and heated in an oven at 80 to 85°C for 18 to 24 hr. In this process the monomers were converted to adsorbed polymer by the benzoyl peroxide initiator without decreasing the iodometric-assayed dibutyl peroxide or Lupersol 101 graft-initiator content. The polymer coatings were also applied by compounding mixtures of kaolin, the monomers, dicumyl peroxide, and polyethylene at elevated temperatures, as described previously [2].

Aluminum and Titanium Acylates

These were applied by either of two methods. In the first, a solution of commercial aluminum isopropoxide or titanium butoxide in dry hexane was mixed with a hexane solution of the particular acid. The resultant acylate solution was then added to a vigorously stirred suspension of kaolin in hexane, and the treated kaolin recovered by rotary evaporation of the solvent. In the second method, a suspension of the kaolin in a solution containing the metal salt and the acid was treated with ammonia or an organic amine to increase the pH of the suspension and precipitate the metal acylate onto the kaolin surface. The treated kaolin was then recovered by filtration and dried in air.

Preparation of Kaolin-Polyethylene Composites

The polyethylene was melted in a Brabender Plastograph roller-mixer at 165°C, the kaolin added, and the mixture kneaded for 10 min at stock temperatures of up to 190°C. The compositions were pressed into 1.2 mm thick sheets for tensile testing or 6 mm thick plates for impact testing, press temperatures of 175°C and times of 5 and 10 min, respectively, being used. The sheets or plates were cooled to room temperature under pressure over a period of 20 min, cut into standard sized specimens, and then stored at 23°C for a minimum of 24 hr prior to testing.

TABLE 1. Mechanical Properties of Kaolin-Polyethylene Composites

Sample No.	Filler or coating composition	Filler loading (% w/w)	Yield stress (kg cm^{-2})	Break stress (kg cm^{-2})	Elongation at break (%)	Impact strength (kg M/M)
	Reference Materials					
1	Unfilled polyethylene	0	289	274	1045	2.77
2	Hydrite 10	20	280	178	218	1.24
		40	292	281	13	0.65
3	Freeport Sulphur "Ox-3	20	285	177	36	1.33
		40	270	254	10	0.83
4	Georgia Kaolin "Kaophobe-5"	20	300	226	29	1.98
		40	278	266	8	1.14
	Hydrite 10 Derivatives[a]					
	Saturated coatings					
5	0.6 n-Hexylamine	20	276	168	291	1.38
		40	276	276	36	0.74
6	5.0 TEAS	20	279	182	162	1.92
7	5.0 TODS	20	272	193	668	1.38
8	2.5 OA-2-ethyl-butyrate	20	269	174	300	1.91
9	3.0 OA-hexoate	20	270	170	152	2.24
10	2.5 OA-sesqui-2-ethylhexoate	20	267	234	26	1.27
11	2.5 OA-laurate	20	274	171	16	1.73
		40	245	241	5	1.38

	Unsaturated coatings					
12	2.0 TEVS	20	293	181	226	1.77
13	2.0 TPMA	20	301	202	277	1.96
14	2.0 TEVS, 3.0 TEAS	20	313	203	71	1.58
15	3.3 OA-oleate	20	272	171	167	1.49
16	1.5 OA-acrylate	20	292	178	150	2.23
17	1.5 OA-methacrylate	20	296	191	420	2.79
		40	325	298	14	2.34
18	1.5 OA-methacrylate, L101	20	301	187	430	3.04
		40	318	310	12	2.51
19	1.5 OA-methacrylate (applied in aqueous medium)	20	305	245	45	1.98
20	1.5 Preformed OA-methacrylate	20	278	198	135	1.83
21	1.5 p-Bis(diallylamino)benzene	20	307	201	152	1.36
22	4.0 Polypiperylene	20	300	216	142	1.32
	Reactive-Polymer Coatings					
23	1.5 BAEMA, 3.0 BDMA, BP	20	273	175	301	2.63
		40	258	258	10	1.96
24	1.5 BAEMA, 3.0 BDMA, BP, DBP	20	274	186	222	2.55
		40	255	255	9	1.98

(continued)

TABLE 1 (continued)

Sample No.	Filler or coating composition	Filler loading (% w/w)	Yield stress (kg cm^{-2})	Break stress (kg cm^{-2})	Elongation at break (%)	Impact strength (kg M/M)
25	1.5 BAEMA, 1.5 BDMA, 1.5 EA, BP, DBP	20	268	195	130	2.25
		40	253	253	7	1.55
26	1.5 BAEMA, 1.5 BDMA, 1.5 MMA, BP, DBP	20	269	192	545	2.17
		40	252	252	9	1.57
27	1.0 MVP, 5.0 BDMA, BP	20	280	175	67	2.84
28	1.0 MVP, 5.0 BDMA, DICUP[b]	20	300	189	356	2.05
29	1.0 MVP, 2.0 EHA, 3.0 BDMA, DICUP[b]	20	303	175	109	1.98
30	1.0 MVP, 4.0 EHA, 1.0 BDMA, DICUP[b]	20	294	187	359	1.90
31	1.0 MVP, 5.0 BDMA, BP, L101	20	306	204	40	1.46
32	0.5 MVP, 3.0 BDMA, BP, L101	20	303	222	68	1.31
33	0.5 MVP, 3.0 DEGA, BP, L101	20	308	203	222	1.89
		40	330	274	24	2.31

[a] The abbreviations for ingredients used in the surface treatments are as follows: BAEMA, t-butylaminoethyl methacrylate; BDMA, 1,3-butylene dimethylacrylate; BP, benzoyl peroxide; DEGA, diethylene glycol diacrylate; DBP, di-t-butyl peroxide; DICUP, dicumyl peroxide; DMAEMA, dimethylaminoethyl methacrylate; EA, ethyl acrylate; EHA, 2-ethylhexyl acrylate; L101, "Lupersol 101," 2,5-bis-(t-butylperoxy)-2,5-dimethylhexane; MMA, methyl methacrylate; MVP, 2-methyl-5-vinyl pyridine; OA-, oxyaluminum-; TEAS, amyl triethoxy silane; TEVS, vinyl triethoxysilane; TODS, octadecyltriethoxysilane; and TPMA, 3-(trimethoxysilyl)propyl methacrylate. The figures listed with the ingredients refer to their percentage content, w/w kaolin. Peroxide contents were each 0.05% w/w kaolin.

[b] Monomers polymerized during compounding process; dicumyl peroxide content 0.1% w/w kaolin.

Evaluation of Treated Kaolins and Their Composites

The rheological properties of paraffin oil suspensions of the kaolins were evaluated as previously described [3], the values for yield stress being derived by application of Casson's method. Tensile properties were determined by standard procedures at a strain rate of 50 cm/min using specimens cut to BS 903, A-2 type E profile (25 mm gauge length). Impact strengths of notched 50 mm x 6 mm bars were measured using a Hounsfield Charpy tester. The listed tensile and impact strengths for each composition are the mean values measured for a minimum of 6 tensile and 18 impact test specimens.

RESULTS

The various treated kaolins were examined for the following properties.

Wetting and Dispersibility in Paraffin Oil

This medium was used in rheological studies as a model for molten polyethylene. The observed yield stress values give an indication of the extent of particle-particle interactions and the degree of dispersion of the kaolins, both of which are dependent on the degree of wetting of the mineral surfaces by the hydrocarbon medium, and on the extent to which electronic edge-face interactions between the kaolin particles are masked; an ideal dispersion would have zero yield stress. The observed yield stresses for paraffin oil dispersions of untreated kaolin, commercial treated kaolins, and our products are listed in Table 2.

Compounding Characteristics

The Brabender mixer torque requirements during mixing yielded information on the ease of incorporation of the kaolins in molten polyethylene. Although surface treatments yielded modest reductions of 5 to 10% in mixing torque, other effects, such as the influence of the kaolin surfaces on the rate of thermomechanical degradation of the polyethylene melt, and graft or curing reactions occurring during the mixing process, were of greater significance. Particular examples will be mentioned later.

Tensile Properties

These properties namely yield stress, stress-at-break, and elongation-at-break are listed in Table 2. The tensile strengths of

TABLE 2. Yield Stresses for 20% w/w Suspensions of Kaolins in Paraffin Oil at 25°C

Kaolins	Yield stress (dyne cm^{-2})
Hydrite 10	>1000
Georgia Kaolin "Kaophobe 5" [a]	4.0
Freeport Sulphur "Ox-3" [b]	5.5
Hydrite 10 kaolin treated with:	
5% Triethoxyoctadecyl silane	23.0
1.8% Oxyaluminum methacrylate	1.4
3.0% Oxyaluminum hexoate	4.3
2.5% Oxyaluminum 2-ethylbutyrate	2.0
1.5% Oxyaluminum sesqui-2-ethylhexoate	1.7
2.5% Oxyaluminum laurate	1.6
3.3% Oxyaluminum oleate	1.6

[a] Complex oleate-treated kaolin.

[b] Oxytitanum oleate-treated kaolin.

the composites were the peak stress values reached during extension of the test specimens; in each case these were also the yield stress values.

Impact Properties

This refers to the impact strengths of the composites which are also listed in Table 2.

The results listed as Nos. 5 to 33 in Table 2 refer only to composites based on high-density polyethylene and on Hydrite-10 kaolin. Other grades of polyethylene and kaolins were also examined, and generally yielded qualitatively similar results to their analogs reported in Table 2. The treated kaolins are broadly grouped in the table according to whether they are:

1. Reference materials; i.e., untreated and commercially treated kaolins.
2. Essentially saturated and unreactive toward free radicals; e.g., alkylamine-, alkyl silane-, or metal alkanoate-treated kaolins.
3. Unsaturated and reactive toward free radicals; e.g., allylamine-, vinyl silane-, or metal alkenoate-treated kaolins.
4. Encapsulated with cross-linked polymer layers containing residual vinylic unsaturation.

DISCUSSION

The kaolin surface contains active sites capable of forming strong donor or salt-like bonds with organic amines and metal cations. In addition, all practical samples contain reactive surface hydroxyl groups which either form part of the crystal lattice or are derived from spontaneous surface hydrolysis in the presence of moisture [4]. These can form strongly bonded condensation products with reactive silanes or metal alkoxides [5], and such reactions can provide complete surface coverage and favorable orientation of the surface-modifying molecules.

Our results show that, while most of the surface treatments could improve the dispersion of kaolin in hydrocarbon media, there is little correlation between such dispersibility and mechanical properties of the corresponding polyethylene composites, although treated fillers with very poor oil dispersibility usually yielded mechanically weak composites.

Saturated Organophilic Kaolins

Treatment of kaolin with saturated reagents generally resulted in an increase in the impact strength and elongation-at-break values of the composites containing 20% w/w filler (equivalent to 8.2% v/v), and a reduction in tensile strength relative to the untreated composite. The use of 40% w/w filler content resulted in decreased elongation-at-break and tensile strength values. These results are similar to those predicted by Nielsen [6] for systems in which there is reduced or no adhesion between the filler and the matrix, and suggest that, while treatment with short-chain saturated reagents may improve the compatibility and dispersibility of the fillers in oil and in polyethylene, these reagents apparently weaken the bonds between the filler and the matrix. The effects of treatment with long chain, i.e., polymeric, reagents which could improve the adhesion of the matrix through intermolecular chain entanglement were not investigated, although treatment with alkyd resins has been recently reported to greatly increase tensile and impact strength of kaolin-filled polyethylenes [7].

Unsaturated Reactive Kaolins

Adhesion between the matrix and filler can be improved by graft formation between the resin matrix and strongly adsorbed, reactive surface species on the mineral. For example, vinyl and methacryloxy silanes and chromium chelates are used for this purpose in the surface pretreatment of glass fiber used in free-radical cured styrene-polyester resins [8]. Free radicals can be readily generated in molten polyethylene either by thermomechanical chain scission during compounding or, more efficiently, by using suitable "high-temperature" initiators such as dicumyl peroxide.

We found that these radicals reacted readily in model systems with polymers bearing pendant vinyl or acrylic groups. The trapping, by graft formation, of such radical species by kaolins treated with unsaturated agents was shown in the Plastograph torque records by the absence of the usual melt viscosity decrease due to thermomechanical degradation of the polyethylene in the mixer. In some systems (e.g., Nos. 13 and 14) increases in melt viscosity, probably due to the formation of kaolin-mediated cross-links, were observed during compounding.

Composites prepared using the reactive kaolins showed increased tensile strength values compared to those of both unfilled polyethylene and the untreated kaolin composites, together with improved impact strengths, properties expected for systems with improved matrix-filler adhesion. In the best of the systems there was also little reduction in the elongation-at-break values compared to that of the unfilled resin, reflecting the increased toughness of the composites. It will be noted that improved mechanical properties could be obtained without the addition of graft initiators such as dicumyl peroxide to the formulation, demonstrating the effectiveness of graft formation through trapping of thermomechanically generated matrix polymer radicals by the reactive filler surfaces.

Kaolins treated with weakly basic unsaturated amines (e.g., No. 21), or compounds such as polypiperylene (No. 22), which could be partially desorbed during compounding, yielded composites which showed increased tensile strengths, but were brittle and had impact strengths little better than that of the untreated kaolin composite. Similarly, incomplete coverage of the kaolin surfaces by a strongly adsorbed unsaturated species, resulting either from application of less than the optimum amount or the use of modified techniques which would give a surface coating consisting of isolated aggregates, resulted in composites which were brittle. Thus complete coverage of the kaolin surface by the oleophilic unsaturated reagent, but not necessarily complete utilization of all the reactive groups, is necessary for maximum reinforcement in these systems.

Polymer-Encapsulated Kaolins

Despite these improvements in adhesion, the interface between the ductile matrix and nonductile filler remains a source of mechanical weakness in the composite, as deformation of the material will result in localized stress concentrations which can rupture the matrix-filler bonds and lead to catastrophic crack propagation. Some alleviation would be expected in practical systems as the restraint on polymer chain motion imposed by the adjacent particle surface results in a zone of increased modulus around the filler particles, and a more even distribution of applied stress at the interfaces.

A zone of intermediate modulus can also be obtained by encapsulating the particles with a suitable polymer. The copolymerization of a strongly basic monomer, such as a vinyl pyridine, and a divinylic monomer, such as diethylene glycol diacrylate, on the kaolin particle forms an adherent, highly cross-linked polymer shell with modulus between that of the filler and the matrix [2], and containing a high proportion of residual unsaturation capable of peroxide-initiated graft formation with the matrix polymer. However, the percentage of monomers indicated in the patent examples [2], typically totaling 3% w/w kaolin, corresponds to an encapsulating polymer layer of only about 30 Å thickness. The effective modulus of such a layer is uncertain, and any concept of a graded cross-link density across such a short distance would be tenuous. In examples in which the coating polymer is formed during the compounding of a dry-blended monomer/peroxide/kaolin mixture with polyethylene, it is probable that the divinylic monomer and the peroxide are desorbed and react independently of the filler surface and adsorbed basic monomer.

A series of different polymer-encapsulated kaolins (Table 2) was prepared using monomer compositions which, by analogy with the corresponding bulk polymerized systems, would yield polymers ranging in moduli from those of hard, highly cross-linked to those of soft, rubbery, lightly cross-linked polymers. Some of the coatings were used without addition of the graft-initiating peroxide (Nos. 23 and 27). It was found that only compositions forming the most-highly cross-linked coatings yielded useful increases in impact and tensile strengths relative to those of the untreated kaolin composite, and at 20% filler content the increases were only similar to those that could be obtained using a simple, unsaturated-reagent pretreatment of the kaolin. Again, significant improvements in mechanical properties could be achieved without addition of graft initiators to the composition. The optimum polymer coating composition (No. 33) yielded further increases in tensile and impact strengths at higher filler loadings, but these could be due in part to modification of the matrix by initiator and residual monomers which could diffuse from the coating during compounding. The polyethylene crystalline contents of these composites were less than those of polyethylene containing treated kaolins without added graft initiators.

Metallo-Acylate Coated Kaolins

Alternative high-modulus saturated and unsaturated coatings can be derived from polymeric inorganic basic salts formed, for example, by the partial hydrolysis of metallic derivatives such as alkoxy-aluminum or alkoxytitanium acylates by residual surface-adsorbed water molecules or hydroxyl groups. Freeport Sulphur Co. has patented the use of triisopropyloxytitanium oleate in the treatment of certain kaolin fillers [9]. However, the oxytitanium acylate coatings are readily hydrolyzed on exposure to moist air and lose the acylate moiety when heated during compounding. The analogous oxyaluminum acylates, on the other hand, are more resistant to hydrolysis and withstand temperatures of up to 250° C without decomposition. Although preformed polymeric oxyaluminum acylates (acylate chains containing more than eight carbons) have been used as dye-affinity promoters in unfilled polyolefins, condensation of the precursor alkoxyaluminum acylates with surface hydroxyl groups for treatment of mineral fillers and, in particular, the use of derivatives containing reactive low-molecular weight acylate ($C < 7$) moieties as covalently-bound potential grafting sites has not been previously reported.

Kaolins with polymeric oxyaluminum methacrylate surface coatings (Nos. 17 and 18) formed by treatment with diisopropoxyaluminum methacrylate showed excellent rheology in paraffin oil, and yielded flexible polyethylene composites with greatly improved tensile and impact strengths, whether or not peroxide was added to promote graft reactions during compounding. The treated kaolin also stabilized polyethylene and polypropylene by preventing excessive degradation during compounding. The alkoxyaluminum reagents, like the commercial alkoxytitanium reagents used by Freeport Sulphur Co., require organic solvents for their preparation and application to the kaolin surfaces, although the solvent can be recovered and recycled.

The treatment of kaolin and other minerals with alkoxyaluminum acylates in the manner outlined in this paper is the subject of a patent application.

Kaolins coated with oxyaluminum methacrylate by treatment in aqueous media (e.g., No. 19) showed inferior rheological and mechanical properties compared to kaolins coated in nonpolar anhydrous media. Coatings prepared in aqueous media would consist of precipitated oxyaluminum methacrylate lacking the covalent bonding, uniform coverage, and favorable, oleophilic molecular orientation of coatings formed by in-situ hydrolysis of adsorbed alkoxyaluminum derivatives. Similarly, inferior mechanical properties were observed for the composite (No. 20) containing a blend of kaolin and an equivalent amount of preformed polymeric oxyaluminum methacrylate.

Our results have shown that good dispersion alone of mineral fillers in the matrix is not sufficient for the reinforcement of polyethylene, but must be accompanied by bonding between the filler and the matrix. A good dispersion of reactive-surfaced fillers can still result in hard but brittle composites unless some adequate mechanism exists for the relief of interfacial stress concentrations. In Ceraplast-filled systems this is achieved by the use of organic polymeric high-modulus encapsulants, and it is possible that the oxyaluminum acylate coatings behave in a similar fashion. However, in the latter case, because of the ionic character of the aluminum-acylate bonds, additional interfacial stress relief could occur through a series of reversible dislocations between adjacent matrix bonding sites.

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