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D. G. Hawthorne[a]; J. H. Hodgkin[a]; B. C. Loft[a]; D. H. Solomon[a]
[a] Division of Applied Chemistry, CSIRO, Melbourne, Victoria, Australia

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Polymerization of Vinyl Monomers on Mineral Surfaces; A Novel Method of Preparing Reinforcing Fillers

D. G. HAWTHORNE, J. H. HODGKIN, B. C. LOFT, and
D. H. SOLOMON

Division of Applied Chemistry
CSIRO
Melbourne, Victoria, Australia

ABSTRACT

A novel method for producing modified mineral fillers is reported: The mineral surface is first made "acidic" and this acidic surface is used to initiate the cationic polymerization of vinyl or preferably divinyl monomers, the residual acidic sites being subsequently neutralized with ammonia or an organic base. During compounding, grafting occurs between the encapsulating polymer layer and the matrix polymer via previously formed peroxidic groups in this layer or via radical attachment at unsaturated centers in the polymer coating. The incorporation of these modified fillers in various grades of polyethylene results in significant improvements in processability and in tensile and impact strength relative to the properties of equivalent composites using untreated or merely hydrophobic fillers.

INTRODUCTION

Polymerization on mineral surfaces is of direct interest in a wide variety of scientific disciplines, ranging from theories on the origin of life, in which it is suggested that polypeptides may have formed by the adsorption and reaction of amino acids on mineral surfaces [1], to the encapsulation of minerals for a number of industrial uses.

This paper is concerned with the polymerization of vinyl monomers on mineral surfaces and with the properties of these modified minerals in polymer composites.

DISCUSSION

The minerals used in polymer composites generally have a hydrophilic surface, and it is widely accepted that the interface between this hydrophilic surface and a hydrophobic polymer is a weakness in composite formulations. Incompatibility at the interface has been invoked to explain many properties of filled polymers ranging from various rheological phenomena to mechanical properties.

Two approaches have been used in designing surface treatments to improve the performance of minerals in composites. First, methods have been developed to render the hydrophilic surface layer organophilic. OX-3 made by Freeport Kaolin is a commercial application of this approach. The dramatic improvements in the flow properties of filler dispersions in oils when the filler surface is made organophilic are demonstrated in Table 1. The yield stress which controls the flow at low shear rates almost disappears, making the flow of the dispersions approximately Newtonian. This great reduction in yield stress is a consequence of the improved compatability of the treated minerals in hydrophic media. It should be noted at this point that the viscosity at infinite shear rate is a function of filler particle size and concentration and is not significantly affected by the consequences of particle-medium interaction; hence no change is expected in the parameter by making the surface organophilic.

The mechanical properties of composites of fillers with organophilic surfaces in polyethylene are shown in Tables 2 and 3. Both the impact strength and elongation at break decrease markedly when untreated kaolin is added to polyethylene while the tensile yield strength is decreased slightly. Organophilic kaolin of the same particle size in high-density polyethylene has improved impact strength, a slight increase in tensile yield strength, and a decrease in elongation at break. The decreased yield strength and increased elongation at break of the hexylamine coated kaolin composite indicate that the hexylamine is acting as a plasticiser, or that the adhesion between the mineral and the polymer is decreased [2].

TABLE 1. Flow Parameters of Filler Dispersions in Oils

Filler	Yield stress (dyne cm^{-2})	Viscosity at infinite shear rate (poise)
A. 20% Filler in paraffin oil at 25.0°C		
Hydrite 10 kaolin, untreated	>1000.0	2.3
Hydrite 10 + decylamine	31.0	2.3
Freeport OX-3	5.5	2.3
Hydrite 10 + linseed oil	0.5	2.0
Hydrite 10 + piperylene	1.5	2.2
Hydrite PX kaolin, untreated	936.0	2.3
Hydrite PX + piperylene	0.2	2.3
Talc, untreated	35.4	3.6
Acidified talc + piperylene	1.4	3.5
B. 30% Filler in linseed oil at 25.0°C		
Hydrite PX kaolin, untreated	114.0	0.5
Hydrite PX + piperylene	58.0	0.8
Hydrite PX + decylamine	48.0	1.3

It is obvious from Tables 2 and 3 that the simple organophilic treatment is not sufficient to produce a composite with properties close to those of the unfilled polymer. The search for even better properties has led to a second class of modified fillers in which additional interaction between the mineral filler and the polymer has been sought. It has been postulated [3, 4] that an intermediate layer which interacts strongly with both the filler surface and the matrix polymer would provide the required improvement. In addition, with suitable unsaturated monomers and initiators in the layer such a system could give a "graded seal," or layer of cross-linked polymer, to facilitate the transfer of stress across the mineral-polymer interface. Chemical bonding of organic entities to the surface hydroxyl groups of the mineral filler is possible but presents many difficulties in designing commercially acceptable systems. The alternative approach of multipoint physical adsorption, as given by a polymer, is therefore of interest.

Interaction between the adsorbed polymer layer and the matrix polymer is claimed to be promoted by the incorporation of residual unsaturation and by the addition of free-radical initiators [4].

Modified fillers of the above type have, in the past, often failed in commercial applications because of the relatively high cost of the

TABLE 2. Mechanical Properties of a Composite Containing 20% Filler in High-Density Polyethylene

	95% Confidence limits for yield strength (kg cm^{-2})	Elongation at break (%)	Impact strength (kg M/M)
No filler	289 ± 4	1300	2.63
Untreated Hydrite 10 (H 10)	282 ± 5	100	1.23
H 10 + 0.6% hexylamine	276 ± 12	260	1.40
Freeport Kaolin OX-3	285 ± 3	40	1.30
Commercial reactive encapsulated kaolin	286 ± 3	25	1.23
SRF Carbon Black	318 ± 2	50	1.00
H 10 + 4% isoprene; NH_3 terminated; oxidized	300 ± 2	90	-
H 10 + 4% β-pipene; NH_3 terminated; oxidized	286 ± 4	90	1.29
H 10 + 4% butyl vinyl ether, NH_3 terminated; oxidized	297 ± 2	140	1.93
H 10 + 4% styrene, NH_3 terminated, ozonized	299 ± 4	45	1.56
H 10 + 4% piperylene, NH_3 terminated, oxidized	300 ± 4	140	1.32
H 10 + 4% piperylene, allylamine terminated; oxidized	307 ± 2	75	1.18
H 10 + 4% piperylene, dimethylaminoethyl methacrylate terminated; oxidized	301 ± 3	150	1.30

free-radical initiators and bifunctional acrylic-type monomers. One other disadvantage of these formulations is the poor efficiency of free-radical initiators on or near a clay surface unless the surface is neutralized. We have shown previously that initiators can be destroyed by acid-induced decomposition reactions on the mineral surface, and that these do not involve free-radical intermediates [5].

We now report on a novel and economical method for coating kaolin-type clays and other minerals with a reactive polymer layer. This process makes use of two observations previously noted in our studies on minerals. The first of these is that styrene and other monomers susceptible to cationic polymerization are readily converted to polymer on minerals with an "acidic" surface [6]. Second, we have noted that nonacidic minerals such as talc can be made acidic by simple coating procedures with inorganic oxides,

TABLE 3. Tensile Properties of a Composite Containing 20% Filler in Low-Density Polyethylene

Filler used	95% Confidence limits for yield strength (kg cm^{-2})	Elongation at break (%)
No filler	90 ± 2	700
Untreated Hydrite 10 (H 10)	96 ± 4	200
H 10 + 4% isoprene[a]	110 ± 3	210
H 10 + 4% piperylene[a]	111 ± 2	140
H 10 + styrene[a]	111 ± 6	190
Freeport Kaolin OX-3	109 ± 1	140
Commercial reactive encapsulated kaolin	96 ± 4	160
SRF Carbon Black	110 ± 1	84

[a] Polymerization NH_3 terminated, polymer oxidized before use.

particularly alumina/silica combinations [7]. Details of the acidic modification of commercial titania pigments are given by Hodgkin and Solomon [8].

As shown in Table 4 for titanium dioxide with an acidic coating, the amount of polymer formed on a particular mineral when excess olefin vapor was passed over the surface was related to the normal ease of cationic polymerization of these monomers. The amount of polymer was also controlled by the monomer concentration and acidity of the surface. In most cases the changes in mineral properties approached a maximum at much lower levels of polymer coating than those shown in Table 4.

In applying these findings to the formulation of reactive polymer coatings which are strongly attached to the mineral surface, one major problem encountered was the large amount of low molecular weight species given by vinyl monomers (e.g., styrene and isobutyl vinyl ether) under conditions commercially acceptable in the mineral industry. For example, at ambient temperature on a kaolin or acidic TiO_2 surface, styrene yields polymers with number-average molecular weights of 500 to 800. This low molecular weight material can be readily desorbed at the temperature of 120 to 180°C used in the compounding of polymers such as polyethylene, polyvinyl chloride, and the common elastomers.

The use of susceptible dienic compounds such as divinyl benzene, divinyl ether, isoprene, and piperylene can overcome this problem and give cross-linked polymer layers which are not readily desorbed. The monomers and reaction conditions can be selected to give an encapsulating polymer layer with residual unsaturation and capable of

TABLE 4. Polymer Yield and Properties on Acidic, Alumina-Silica Coated Titania

Monomer used	Maximum[a] polymer yield (%)	Polymer properties
Isobutylvinylether	6.1	Mostly low molecular weight, soluble
Piperylene	4.7	Higher molecular weight, ~50% soluble
Isoprene	3.5	High molecular weight, ~50% soluble
Butadiene	2.5	High molecular weight, mostly insoluble
Styrene	0.85	Low molecular weight, ~700, soluble
Propylene	0.35	Insoluble; molecular weight unknown

[a] Determined by carbon analysis.

yielding adsorbed peroxide species by aerial autoxidation or mild ozonolysis. The rates of autoxidation of such adsorbed layers are markedly dependent on the nature of the underlying mineral surface, and these observations will be reported in detail in a later communication. Peroxidic cross-linked layers can also be formed by autoxidation of adsorbed monomers or prepolymers containing allylic or polyene groups; for example, the natural drying oils such as linseed oil and their derivatives.

Irrespective of the method of formation, these peroxides decompose during compounding to free radicals which graft the adsorbed coating to the matrix polymer. The ability of such free radicals to initiate grafting reactions with the matrix polymers can be readily demonstrated by model experiments using acrylic monomers. Also IR spectroscopic examination of the nonextractable or fractionated polymeric components of the compounded materials reveals the presence of grafted polymer.

The peroxide content of selected piperylene and linseed oil treated kaolins at various stages of autoxidation and storage are shown in Table 5. Also shown in Table 5 are the tensile properties of composites containing 20% of the kaolin in high-density polyethylene. It can be seen from this table that tensile properties generally improve with increased peroxide content.

TABLE 5. Peroxidation of Coated Hydrite 10 and Its Effect on Tensile Properties of a Composite Containing 20% Filler in High-Density Polyethylene

Time of exposure	Peroxide assay (μequiv/g)	Tensile properties of composite: Yield strength (kg cm^{-2})	Tensile properties of composite: Elongation at break (%)
4% Piperylene on Hydrite 10; aerial oxidation at 20°C			
1 hour	33	297	182
3 days	46	313	160
5 days	90	312	280
4 months	42	308	50
5% Linseed oil on Hydrite 10; oxidation in oxygen at 30°C			
24 hours	175	311	28
48 hours	78	305	20
1 month	35	Filler aggregated	

Some initial difficulties were experienced in preventing color development when coated minerals were used in light colored composites. This problem apparently arises from the residual acidity of the mineral surface as the colors were typical of those expected for carbonium ion formation which would be facilitated under the anhydrous conditions in polymer processing. Neutralization of the acidity by ammonia or organic bases, particularly amines, prior to compounding, minimizes or avoids the color development. Neutralization also helps minimize other unwanted side-reactions, notably acid-induced decomposition of the peroxidic species on storage, and depolymerization of the encapsulating polymer during the compounding processes. Unsaturated amines, e.g., allylamine and aminoalkyl methacrylates, are useful neutralizers and can also participate in grafting reactions during compounding.

The incorporation of these modified fillers in various grades of polyethylene resulted in significant improvements in processability, and in tensile and impact strengths of the composites, over the equivalent composite using untreated fillers, although greater improvements, particularly in impact strength, could be obtained by using the more expensive procedures described in the following paper by Hawthorne and Solomon [9]. The tensile and impact properties of the composites containing 20% w/w of modified kaolins (both commercial and experimental) in high-density polyethylene are summarized in Table 2. Table 3 contains the properties of composites based on low-density polyethylene.

EXPERIMENTAL

Materials

The beneficiated kaolins, Hydrite 10 and Hydrite PX, were donated by the Georgia Kaolin Co.; B.P.C. grade talc was coated with silica-alumina by the method described in the preceding paper [8]. Monomers and solvents were of laboratory reagent quality and were used without further purification. OX-3 kaolin with an organophilic coating was supplied by Freeport Kaolin Co. It has the same average particle size as Hydrite 10.

Polymerization of Monomers on Acidic Mineral Surfaces

The polymerization apparatus consisted of a rotating evacuable 500 ml ribbed flask with attached reservoir for the liquid monomer. The mineral (100 g), previously activated by heating at 110 to 120°C in an air oven for 12 to 24 hr [6], was placed in the flask which was then evacuated. Monomer vapor (4 g for a typical reaction) was then admitted from the reservoir and the flask rotated to tumble the mineral powder through the vapor. The onset of polymerization was indicated by the appearance of a bright coloration typical of active carbonium species. The flask was maintained at 10 to 25°C during the polymerization, and when all the monomer had disappeared (reaction time ~4 hr) the carbonium species were destroyed by the addition of aqueous ammonia (0 to 1 ml, specific gravity = 0.880), or organic amine vapor or solution.

Monomers of low volatility were applied by addition to a suspension of the activated mineral (100 g) in dry hexane (300 ml). After completion of the reaction (about 1 hr for 5% styrene) the pigment was recovered by removal of hexane in vacuo. Linseed oil was applied by addition of the oil to a suspension of activated mineral in hexane followed immediately by hexane removal in vacuo.

Oxidation of Polymer Coatings

Peroxidation of the polyisoprene, polypiperylene, and linseed oil coatings occurred spontaneously when the minerals were exposed to a current of dry air at 20 C. More rapid oxidation occurred if the freshly coated minerals were placed in an oxygen atmosphere. The polystyrene coatings did not yield appreciable peroxide species on aerial oxidation, even using heat or catalysts, an observation supported by a recent publication [10]. However, a brief exposure to ozonized oxygen ($\sim$25 meq/100 g of 5% coated kaolin) resulted in the formation of comparatively stable peroxide species (80 μeq/g kaolin; half-life about 4 days at 20°C) suitable for graft initiation. The peroxide contents were determined by iodometric titration using acetic acid as solvent [5].

Evaluation of Coated Minerals

The flow properties of mineral dispersions in paraffin and linseed oil [11] and the compounding and mechanical properties of mineral-filled polyethylene composites [9] were determined as previously described.

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