

Characterization of Spinel and Hydrated Spinel-Filled ABS: Antioxidant Effect and Strength Properties

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SYNOPSIS

Differential thermal analyses (DTA) were conducted on spinel-filled and hydrated spinel-filled acrylonitrile-butadiene-styrene (ABS) terpolymer. Spinel and hydrated spinel displayed antioxidizing properties in the ABS composite. The enthalpies of oxidation for ABS, spinel-filled ABS, and hydrated spinel-filled ABS were 130, 15, and 0 J/g, respectively. Mechanical property measurements show that hydrated spinel reinforcing properties equal that of precipitated calcium carbonate treated with zinc stearate. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) is a family of terpolymers that contain rubber phases in a styrene-acrylonitrile copolymer (SAN) matrix. Polybutadiene rubber grafted to SAN provides good adhesion between the two phases. ABS is one of the first commercially successful polymer alloys, the three major components of which bring different sets of interesting properties: acrylonitrile provides thermal stability and chemical resistance, butadiene provides impact resistance, and styrene provides rigidity.¹

The thermal oxidative degradation of ABS differs for each of its components. The rate of oxidation of polybutadiene, styrene-acrylonitrile copolymers, and ABS have been compared.^{2,3} It has been observed that the rubber phase of ABS oxidizes more rapidly than the SAN matrix. Infrared experiments have shown that the double-bond peak corresponding to the polybutadiene component disappears and that carbonyl and hydroxy functions appear. Cross-linking of the rubber phase reduces impact resistance of ABS, whereas no significant change of the nitrile or phenyl groups have been detected. A linear relationship exists between the butadiene content and impact strength.⁴ Therefore the degradation of ABS

is assumed here to be caused by oxidation of the butadiene component.

Previous studies suggested that embrittlement of the polybutadiene chains may not be the only factor leading to mechanical property changes.⁵ Oxidation of the grafted polybutadiene component can cause a chain-scission process, resulting in the detachment of grafted SAN copolymer and therefore in the deterioration of impact properties.

ABS may be filled with glass fibers up to 40 wt %. Some nonfibrous fillers such as mica, talc, and calcium carbonate offer high flexural modulus. Pigments, particularly titanium dioxide, may also be added to give whiteness and opacity.

Incorporation of magnesium hydroxide in ABS increases flame resistance and reduces smoke emission.⁶ A similar behavior has been observed with polystyrene.⁷ The fire retardancy and smoke suppression effects are caused by a combination of factors:

1. endothermic decomposition of hydroxides absorbs heat from the polymeric matrix and releases water vapor that then dilutes the fuel in the gas phase;
2. char formation better insulates the substrate from the flame; and
3. the filler acts as a polymeric matrix diluent.

Moreover, alumina and aluminum hydroxide are among the most widely used flame retardants for plastics.⁸⁻¹⁰ They are also effective as smoke sup-

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pressants. Finally, it has been established that combinations of alumina trihydrate and magnesium hydroxide produce less smoke than compounds filled with either loading by itself.¹¹

Because of the flame retardant and smoke suppressant properties of aluminum and magnesium compounds, it was decided to study the antioxidative behavior of spinel, MgAl_2O_4 , and hydrated spinel, $\text{MgAl}_2(\text{OH})_8$, in ABS. Two properties have been investigated: oxidation phenomena below 250°C and strength properties at room temperature. Spinel is a natural mineral (mixed metal oxide) and can be synthesized by numerous methods.¹² Mechanical properties of spinel and hydrated spinel-containing ABS were also studied and compared with those of titanium dioxide and precipitated calcium carbonate-filled ABS.

EXPERIMENTAL

Materials

ABS, Cicolac GSE, originally manufactured by Marbon, was provided as pellets by Borg-Warner Chemicals. The pellets were either ground through a 20-mesh screen in a Wiley mill or, as in the case of the material mixed in the Brabender, were used as is. The starting material for the spinels, aluminum isopropoxide and magnesium ethoxide, were provided by Alpha Products-Thiokol.

Precipitated calcium carbonate, called Super-Pflex 200, was obtained from Pfizer. Super-Pflex 200 is surface treated with zinc stearate and has an average particle size of approximately $0.5\ \mu\text{m}$. It was developed specifically as a reinforcing agent for plastic and rubber compounds. Titanium dioxide, anatase ATX grade, was provided by Tioxide Canada and has a median particle size of approximately $0.2\ \mu\text{m}$.

Preparation of Hydrated Spinel and Spinel

Spinel and hydrated spinel were prepared in our laboratory using a modified sol-gel process developed initially for the preparation of complex perovskite-type compounds.¹² Sol-gel synthesis of mixed metal oxides consists of formation of an amorphous gel from solutions and dehydration at relatively low temperatures. This first step may be followed by a sintering step to crystallize the filler. The most advantageous characteristics of this method are high purity, ultrafine size particles, and excellent control

of the composition of the resulting mixed oxide filler.¹³

Aluminum isopropoxide (53 g) and magnesium ethoxide (15 g) were mixed in a 2 : 1 Al : Mg molar ratio in a flask containing 2.0 L toluene and 0.3 L isopropanol. The mixture was refluxed at 90°C with aid of an oil bath under a carbon dioxide atmosphere until complete dissolution of the magnesium ethoxide. Carbon dioxide facilitated the dissolution of magnesium ethoxide through the formation of magnesium carbonate groups. A solution of 60 mL water and 140 mL isopropanol was slowly added to the stirred mixture to hydrolyze the mixed alkoxides. The resulting precipitate was filtered and placed in an oven at 110°C overnight. The 28-g weight of product obtained corresponds to a quantitative yield of the mixed magnesium and aluminum hydroxides, $\text{MgAl}_2(\text{OH})_8$. A portion of this compound was then heated at 750°C for 2 h to give spinel MgAl_2O_4 . Since the drying step leads to agglomerate formation, the spinel samples were ground in a 2 in. Sturtevant Micronizer fluid energy mill for 30 min.

ABS Composites

Composites used for DTA measurements were prepared from solutions as follows: ABS (270 mg) and filler (30 mg, 10 wt %), were dissolved and dispersed in 20 mL tetrahydrofuran. After the mixtures were made homogeneous by heating and mixing for 1 h, they were poured into Petri dishes, loosely covered and allowed to stand overnight at ambient temperature in order to evaporate a majority of the solvent. The product films were placed in a vacuum oven at 60°C for a minimum of 2 days to remove any traces of solvent. Composites used for mechanical tests were prepared by mixing in a Brabender PL-2 apparatus. Filler, 10 wt %, was added to ABS pellets and mixed at 195°C for 10 min. An antioxidant, 0.2 wt % IRGANOX B561 from Ciba-Geigy, was added before mixing. The pure ABS sample used 300 mg.

Methods

DTA measurements were carried out on a CSI-Stone apparatus, model A501. Weighed samples of at least 5 mg were placed in crucibles and sealed. The crucibles were punctured in a helium atmosphere to allow good contact with helium and release of trapped air. The apparatus was calibrated using the following three standards: *p*-hydroxybutyrophenone, m.p. 93°C ; indium, m.p. 156°C ; and *p*-hydroxybenzoic acid, m.p. 214°C .

Two runs were performed during the analysis. The first was to 150°C to allow for some further mixing of the ABS and filler and to remove traces of solvent and impurities. The second run was to 250°C. The temperature increase was set to 5°C/min with a chart speed of 1 cm/min. The sensitivity of the DTA apparatus was 50 μ V with a chart sensitivity of 10 mV for the sample and 5 mV for the temperature.

The enthalpies of degradation of the samples were calculated from the exothermic peak areas of the DTA curves. Tensile properties of the composites were tested according to ASTM D638 standard. The test samples were prepared by compression molding at 195°C. Tests were performed on an MTS 810 Material Test System at room temperature. The distance between the jaws was 75 mm and the elongation rate was equal to 5 mm/min.

X-ray spectra were determined with a Scintag XDS 2000 diffractometer, equipped with a Tektronik Micro Vax 2000 computer. The micrographs were obtained with a Jeol JSM-35 scanning electronic microscope.

RESULTS

Figure 1 shows the X-ray spectra of the spinel filler prepared by the sol-gel method and heated at 750°C for 2 h. The six peaks recorded correspond to the spinel lattice, as seen on the spinel pattern. Therefore, it may be assumed that the spinel prepared in our laboratory is pure and highly crystalline.

Figure 2 presents pictures of spinel [Fig. 2(A,B)], titanium dioxide [Fig. 2(C)] and precipitated calcium carbonate [Fig. 2(D)]. The spinel is made up of agglomerates [Fig. 2(A)] and free particles [Fig. 2(B)]. In both cases the ultimate particle size is about 30 nm whereas the size of agglomerates may reach 1 μ or even more. However, agglomerates larger than 1 μ are relatively rare. On the other hand, TiO₂ and precipitated calcium carbonate (PCCD) particles are relatively uniform and do not form strong agglomerates [Fig. 2(C,D)].

DTA measurements are presented in Figure 3 and Table I. The softening point shifts toward higher temperatures for the three samples in the second run. This may be related to elimination of residual

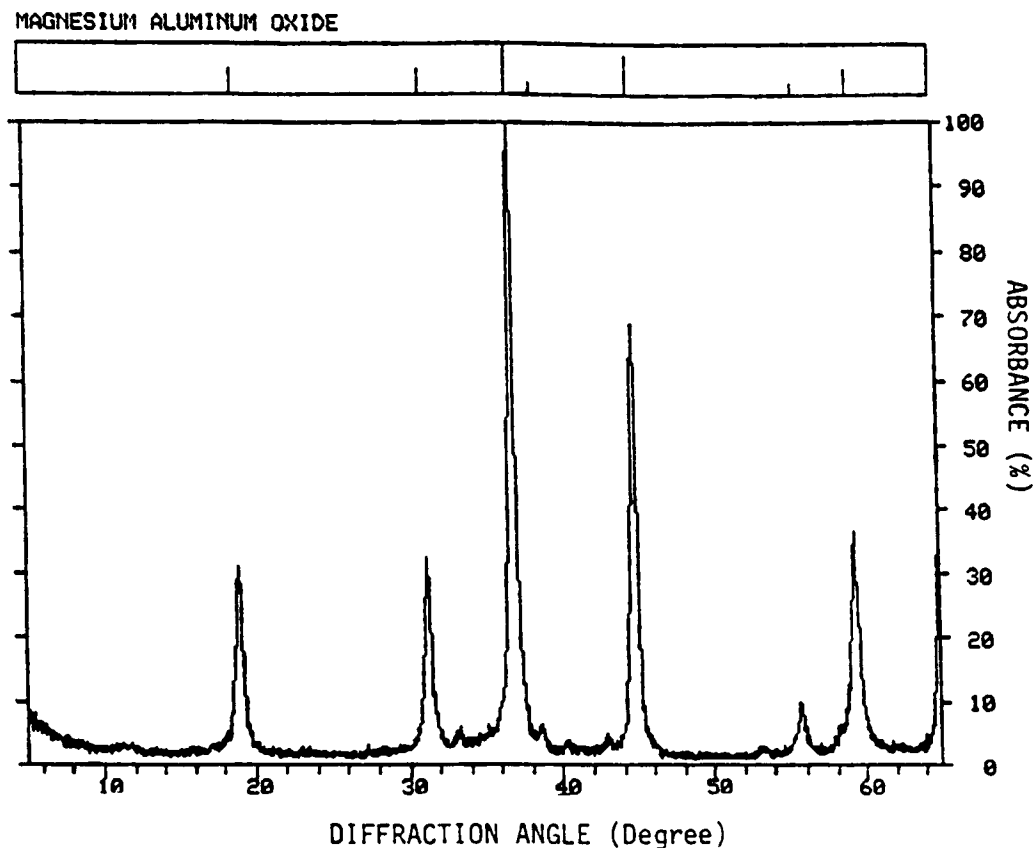


Figure 1 X-ray diffraction spectra of spinel filler. The pattern on the top shows the computerized peaks of spinel.

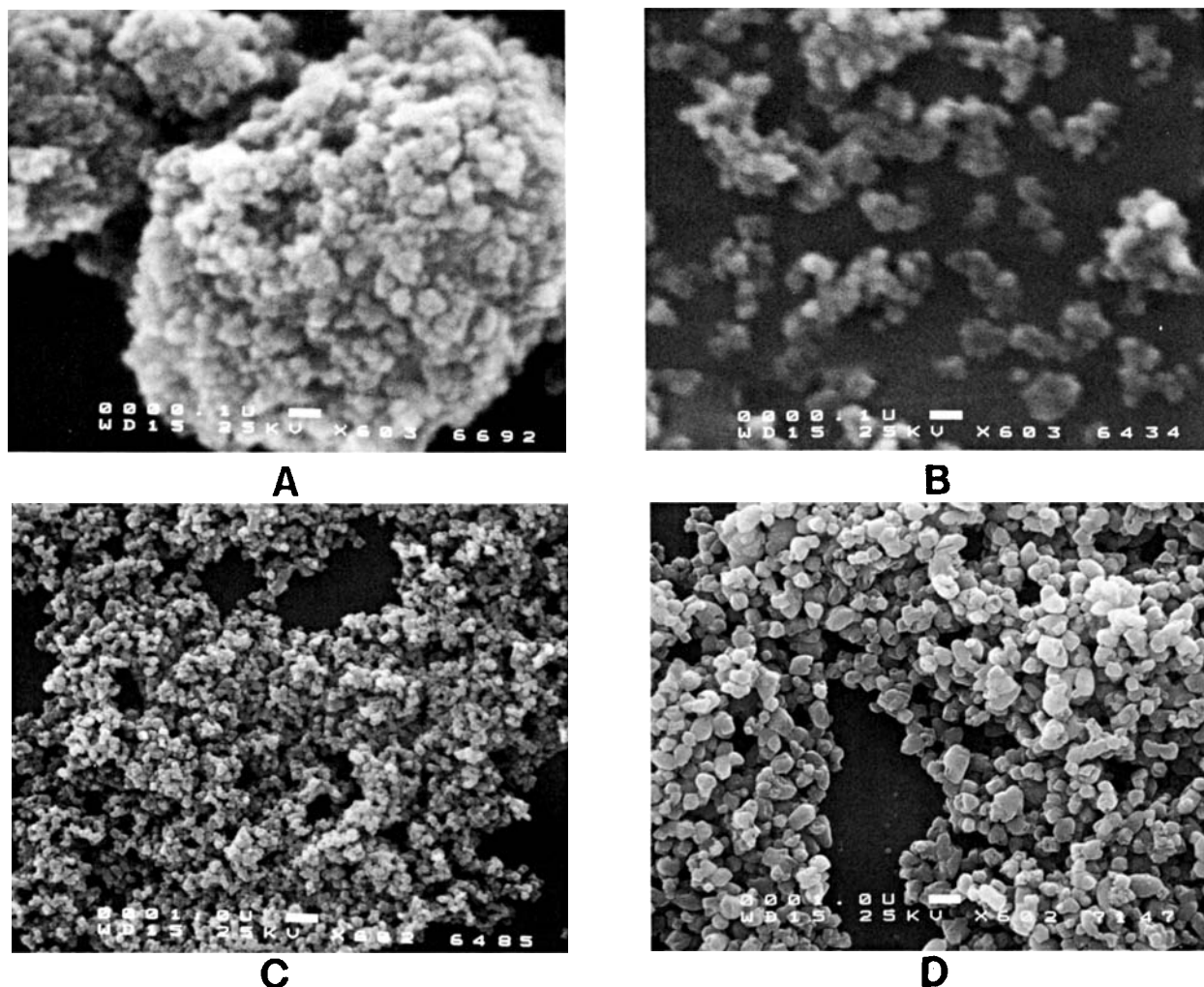


Figure 2 Micrographs of fillers. (A) agglomerates of spinel primary particles; (B) free primary particles of spinel; (C) titanium dioxide particles; (D) precipitated calcium carbonate particles. Magnification: (A) and (B) $\times 6000$; (C) and (D) $\times 6000$.

solvent or impurities that act as plasticizers during the first heating run. However, the effect of the fillers cannot be detected from the softening point temperatures that reach 96–97°C in each case.

An exothermic peak is recorded around 130°C for pure ABS in air whereas no peak is detected in helium. Therefore, it may be assumed that this peak corresponds to the thermal oxidation of the butadiene microphases, of which the enthalpy of oxidation can be evaluated to be around 130 J/g.

Spinel-filled ABS exhibits an oxidation peak at 183°C, that is, a shift of more than 50°C as compared with pure ABS. Moreover, the value of the enthalpy of oxidation is approximately ten times lower. Spinel may thus be considered to act as an antioxidizing agent. This antioxidizing effect is even more evident

in the case of hydrated spinel since no oxidation peak is detectable.

Mechanical property measurements of filled ABS samples are indicated in Figures 4 and 5. The relative value of Young's modulus of hydrated spinel-filled ABS is comparable to PCC-filled ABS that presents an improvement of 20% with respect to neat ABS (Fig. 4). In the same way, relative values of elongation at break of ABS filled with PCC and hydrated spinel are comparable (around 75%). An improved Young modulus associated with a reduced elongation at break suggests a good dispersion and/or interaction between the fillers and the polymeric matrix. However, spinel- or titanium dioxide-containing ABS leads to intermediate results between the pure ABS matrix and that of hydrated spinel-filled or

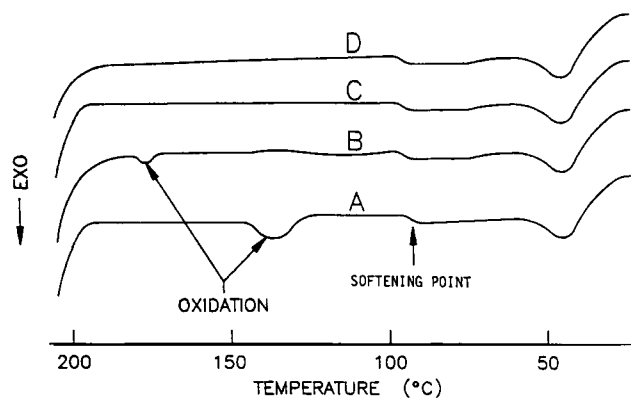


Figure 3 Thermograms of pure ABS in air (curve A). A large oxidation peak is observed at 129°C. Spinel-filled ABS thermogram presents a small oxidation peak at 183°C (curve B) whereas hydrated spinel-filled ABS does not exhibit any oxidation peak (curve C) such as with pure ABS in an inert atmosphere (curve D).

PCC-filled ABS. It shows that the adhesion between spinel or titanium dioxide and ABS is weaker than between hydrated spinel or PCC and ABS.

DISCUSSION

Spinel and hydrated spinel have been shown here to act as antioxidizing fillers for ABS. The hydrated form seems to be more efficient than the oxide for two reasons. First, the hydrated spinel was not sintered, therefore its density is lower (ca. 2.4 g/cm³) than that of spinel (3.5 g/cm³). This means that 10 wt % of hydrated spinel fills more space in the ABS matrix than 10 wt % spinel. Consequently, the surface of interaction between the filler and the polymer is larger in the former and the antioxidizing phenomena is augmented accordingly. Second, the

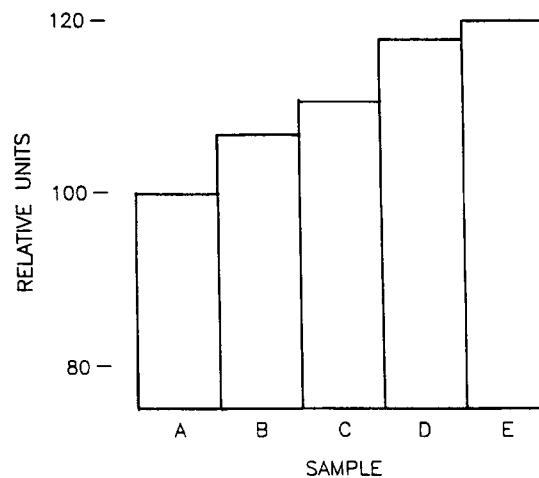


Figure 4 Young's modulus of 10% filler containing ABS: (A) pure ABS; (B) spinel filled; (C) titanium dioxide filled; (D) hydrated spinel filled; (E) PCC filled.

sintering step leads to the formation of agglomerates. These agglomerates, which are denser than those observed after the drying step, reduce the degree of dispersion of the spinel in the polymeric matrix and, therefore, the interaction between the two phases.

The antioxidative effect of spinel and hydrated spinel seems to be caused by their two components: magnesium and aluminum oxides or hydroxides. In regard to the magnesium component, it has been shown that the temperature of maximum weight loss of polystyrene/decabromobiphenyl oxide/magnesium hydroxide systems is shifted toward the higher temperatures with respect to the polystyrene/decabromobiphenyl oxide system.⁷ This shift in high temperature oxidative stability exceeds 30°C on addition of magnesium hydroxide. Such an effect also is observed with the polybutadiene component of ABS (Table I and Fig. 3).

Table I DTA Measurements

| Sample | Run | Softening Point Temperature (°C) Air | Oxidation Temperature (°C) | | Enthalpy of Oxidation (J/g) |
|------------------------|-----|--------------------------------------|----------------------------|----|-----------------------------|
| | | | Air | He | |
| Pure ABS | 1 | 69 | 132 | — | 130 |
| | 2 | 96 | 129 | — | |
| Spinel-filled | 1 | 78 | > 150 | — | 15 |
| | 2 | 97 | 183 | — | |
| Hydrated spinel-filled | 1 | 81 | > 150 | — | 0 |
| | 2 | 96 | N/D | — | |

N/D, not determined.

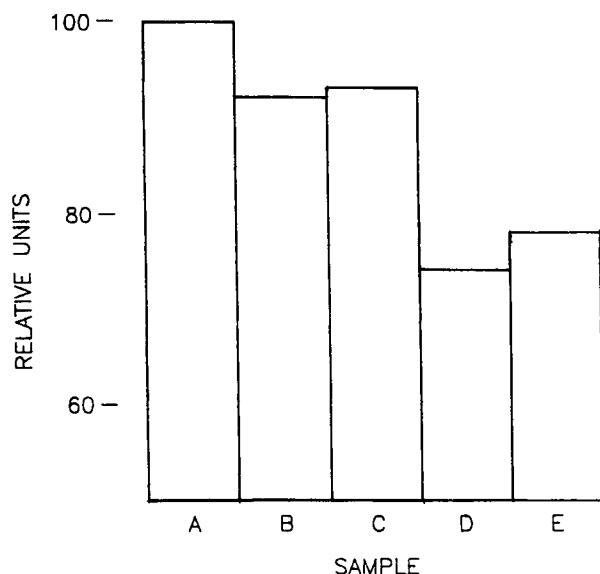
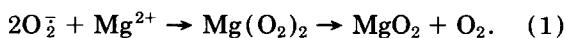


Figure 5 Elongation at break of 10% filler-containing ABS. (A-E) see Figure 4.

Kelleher has shown that the oxidation of ABS at 140°C occurs in the polybutadiene phase.³ This thermally initiated degradation in the presence of oxygen proceeds by an autocatalytic free-radical mechanism.¹⁴ The primary products of thermal oxidation are hydroperoxides that result from the reaction between singlet oxygen (¹O₂) and double bonds.¹⁵ These hydroperoxides, in turn, thermally decompose to generate radicals that are further oxidized by molecular oxygen. The decrease in magnitude and shift to higher temperatures of the exothermic peak (130°C for ABS) on filling with spinel or hydrated spinel may be caused by a slowing of oxidative degradation in the presence of magnesium compounds, as has been observed in the case of cellulose.¹⁶

As an explanation for the antioxidative effect observed with cellulose in the presence of magnesium salts, it has been postulated that magnesium ions promote dismutation of superoxide radicals by the following reaction:¹⁶



Superoxide radicals are formed by the action of oxygen with hydroperoxides. The action of magnesium compounds on superoxide radicals has been confirmed by electronic paramagnetic spectroscopy measurements.¹⁷ The latter show that magnesium compounds such as magnesium sulphate or magnesium hydroxide decompose superoxide radicals by forming a stable magnesium superoxide complex

that slowly decomposes to magnesia, as indicated in eq. (1).

Young's modulus and elongation at break of filled ABS show that spinel and hydrated spinel improve strength properties of pure ABS. Moreover, hydrated spinel is a better reinforcer than spinel and reaches the reinforcing level of zinc stearate surface modified PCC. The difference between spinel and hydrated spinel is also caused by, at least to some extent, the different morphology of both fillers as discussed before:

1. the lower density of hydrated spinel leads to a larger specific surface that produces more interactions with the matrix; and
2. hydrated spinel contains less agglomerates than spinel thus allowing the dispersion of filler particles to be more uniform.

It is also interesting to note that ultrafine fillers are of considerable interest for elastomers such as rubber, nitrile rubber, or styrene-butadiene rubber because a very strong dependence exists between the degree of reinforcement and the particle size.¹⁸ Fillers having particle sizes larger than 1000 nm may be considered as "diluent fillers," whereas "semi-reinforcing fillers" and "reinforcing fillers" have particle sizes between 100 and 100 nm, and between 10 and 100 nm, respectively. The spinel and hydrated spinel prepared in our laboratory have a primary particle size of 30 nm, although agglomerates of 100 nm may be found. Therefore, it may be assumed that the removal of these agglomerates would lead to a considerable improvement of the reinforcing effect. Nevertheless, it has been previously observed that spinel is characterized by an acidic surface¹⁹ whereas hydrated spinel is an acid receptor. Since ABS has the properties of a Lewis base, we may assume that, for the same surface of interaction polymer/filler, spinel should provide a better adhesion than hydrated spinel.

CONCLUSIONS

These results show that spinel and especially hydrated spinel present interesting properties in ABS:

1. antioxidant effect around 150°C;
2. reinforcing effect; and potentially
3. flame retardancy and smoke suppressant effect.

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