

Distribution of Calcium Carbonate and Silicone Elastomer in a Flame Retardant System Based on Ethylene–Acrylate Copolymer, Chalk and Silicone Elastomer and Its Effect on Flame Retardant Properties

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ABSTRACT: A combination of microscopy studies (SEM, ESEM/EDX, and TEM/EDX) is proven to be useful in locating chalk particles and silicone elastomer in a flame retardant system based on ethylene–acrylate copolymer, chalk, and silicone elastomer. The dispersion of the two additives was also obtained. The chalk particles were visually observed (at a certain degree of magnification), and the silicone elastomer was detected using characteristic X-ray mapping and line scans. The analysis provided a good contrast between chalk particles and silicone elastomer in the sur-

rounding polymer matrix. It is shown that dispersion of the additives depends on the mixing conditions, where tougher mixing conditions improve dispersion. A discussion is given on how dispersion correlates with the flame retardant properties of this system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2085–2095, 2006

Key words: additives; dispersions; electron microscopy; flame retardance

INTRODUCTION

As a result of environmental and safety issues having to do with flame retardants based on halogens, much attention has been given in the two past decades to halogen-free flame retardants. Most halogen-free formulations for manufacturing standard cables are based on inorganic fillers such as aluminum hydroxide and magnesium hydroxide. With hydroxides, a high filler loading is needed to obtain sufficient flame retardancy, and this can create problems with melt processing. An alternative halogen-free flame retardant system was developed in the early 1990s.¹ This is based on ethylene–acrylate copolymer, chalk and silicone elastomer, where less filler is needed to obtain a good flame retardant effect while maintaining good production speed and acceptable cost.

Studies on inorganic systems show the importance of a good dispersion of filler in the matrix to obtain an optimal flame retardant effect and optimal product

performance. Dispersion correlates with mixing, which is known to depend on a number of factors, such as the amount, size, structure, orientation, and cohesivity of the fillers and its agglomerates, filler/agglomerate–polymer interactions, choice of polymer, and mixing equipment and its processing parameters (screw speed and geometry, temperature profile, strength of the applied flow field, and mixing time). Hornsby et al. have studied how dispersion is affected by the compounding process and the influence of operating variables, filler characteristics (calcium carbonate filler), and the polarity of the thermoplastic matrices (polypropylene and nylon 6,6) in relation to particle-agglomerate formation and breakdown.² State of dispersion (fraction of agglomerates) has been characterized by Suetsugu et al. for calcium carbonate filled polypropylene model composites processed at various mixing conditions. Correlations between dispersion and different mechanical properties were obtained.³ An understanding of the differences between a good and a poor mixture is often difficult to describe on a macroscopic, quantitative basis. Poor mixing may promote loss of material performance and, consequently, premature product failure, but mixing that is too good may provide the same bad results. Generally, optimum mixing conditions are required for each material and each production process.

Many methods are available for assessing dispersion quality, where most depend on microscopy for

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TABLE I
Formulations and Processing Conditions

Material	CaSiEBA-X min	CaSiEBA-com
Ethylene butyl acrylate [EBA]	57.3	57.3
Chalk [CaCO ₃]	30.0	30.0
Silicone elastomer master batch	12.5	12.5
Antioxidant	0.2	0.2
Manufacture	Two-roll mill	Full scale extruder
Mixing time [X] (min)	4, 10, 20, 30	–
Temperature (°C)	180	–

visualizing the state of dispersion of fillers and other additives. Microscopy combined with advanced image analysis methods also offers a great potential for studying dispersion characteristics. Mills et al. proposed an alternative method for quantitative assessment of dispersion quality based on the classification of X-ray map data, using multifractal spectrum analysis,⁴ originally a technique used for the investigation of probability distributions generated from model simulations or experimental data.⁵ By combining scanning electron microscopy with energy dispersive X-ray and multifractal image analysis, Mills et al. found that a polymer composite of ethylene vinyl acetate random copolymer containing 60 wt % of magnesium hydroxide had a better dispersion than that of a 30 wt % composite, most likely as a result of higher melt viscosity.

This study investigates the location and dispersion of chalk particles and silicone elastomer in an ethylene-acrylate copolymer matrix, at a mostly microscopic level, as it is believed that dispersion correlates with the flame retardant properties.⁶ The location of silicone elastomer in respect to the chalk particles is of special interest. Two materials produced at different mixing conditions on a laboratory two-roll mill as well as a material produced in full scale are analyzed with microscopes (scanning electron microscope and transmission electron microscope) equipped with energy dispersive X-ray spectrometer.

EXPERIMENTAL

Materials and sample coding system

The material formulations and processing conditions are given in Table I. The denomination CaSiEBA is based on the abbreviations of the individual components, where Ca stands for chalk, Si stands for silicone elastomer master batch, and EBA stands for ethylene butyl acrylate. Further, the abbreviations 4 min, 10 min etc. correlate to the mixing time of the material and the abbreviation com correlates to commercial material.

CaSiEBA-4 min, CaSiEBA-10 min, CaSiEBA-20 min, and CaSiEBA-30 min were produced on a laboratory two-roll mill at 180°C for 4, 10, 20 and 30 min, respectively. (The rotation speed was 5 rpm during addition of fillers and, thereafter, 22 rpm, on both rolls.) Polymer and antioxidant were first added, followed by the addition of chalk, and finally of the silicone elastomer master batch. The foils were pelletized using a Rapid granulator, providing coarse granules. CaSiEBA-com was manufactured in a 300 mm/7D Buss-co-kneader and provided by Borealis Polymers Oy, Finland.

Fire tests

The oxygen index was determined with a Stanton Redcroft FTA Flammability Unit, according to ISO 4589.⁷ The results are based on 10 test specimens (150 × 6 × 3 mm³). The test specimens are stamped out from a compression molded plate pressed in a Collin 300 Press by applying low pressure (20 bar) at 150°C for 1 min, followed by high pressure (200 bar) for 5 min at the same temperature. The cooling rate was 10°C/min under high pressure.

A Stanton Redcroft cone calorimeter was used to obtain results, such as the rate of heat release, total heat release, ignition time, burning time, and weight loss. Test specimens (100 × 100 × 3 mm³) obtained from a compression molded plate (same procedure as above) were exposed to a heat flux of 35 kW/m² and an airflow of 24 L/s, according to ISO 5660 part 1.⁸ The results are based on three tests except for CaSiEBA-20 min, which is based on six tests.

Analytical methods including sample preparation

Microtome cutting

A granule of a pellet (CaSiEBA-com) and coarse granules (CaSiEBA-4 min and CaSiEBA-20 min) were cut with a Leica AB Supercut 2065 microtome cutter (nitrogen cooling at –50°C) to obtain 0.2-μm-thin slices.

Scanning electron microscopy

Scanning electron microscopy (SEM) imaging (secondary electrons) was done using a Jeol JSM 5300. The microscope was operated at 20 kV. Images with a magnification of ×3000 were obtained. The surface of the specimens was obtained through fracturing in liquid nitrogen. The surfaces were coated with gold before analysis.

Environmental scanning electron microscopy (ESEM/EDX)

ESEM imaging was done on thin slices using an ElectroScan 2020 Environmental Scanning Electron Micro-

TABLE II
Oxygen Index Data

Material	Mixing time (min)	OI
CaSiEBA-4 min	4	31.5
CaSiEBA-10 min	10	32.0
CaSiEBA-20 min	20	34.0
CaSiEBA-30 min	30	32.5
CaSiEBA-com	–	38.0

scope equipped with a Link eXI Energy Dispersive X-ray Spectrometer (EDX). The microscope was operated at 20 kV for secondary electrons (SE) imaging ($\times 4000$) and at 10 kV for EDX analysis (line scans and X-ray mapping). SE images were used to analyze the dispersion of chalk particles (morphology), and EDX analysis was used to obtain elemental information on calcium and silicon atoms. Mapping was performed for 1 h.

Transmission electron microscopy (TEM/EDX)

Thin slices were studied in a 200 kV Philips CM 200 FEG (Field Emission Gun) TEM equipped with a Link ISIS EDX. The aim and procedure are similar to those in ESEM, but a greater magnification was used during the analysis. Mapping was performed for 2 h.

RESULTS

Flame retardant tests

Nonflame retardant polyolefins, such as low-density polyethylene (LDPE) and ethylene butyl acrylate copolymer (EBA), have an oxygen index value between 17.0 and 18.0.^{9,10} Adding chalk and silicone elastomer to EBA, i.e., CaSiEBA, increases the oxygen index substantially.¹¹ CaSiEBA produced on a full scale (CaSiEBA-com) have a value of 38, while materials produced on a laboratory two-roll mill (CaSiEBA-4 min, CaSiEBA-10 min, etc.) have lower values, as seen in Table II.⁶ The oxygen index of materials produced on the two-roll mill is influenced by mixing time, where a mixing time of 20 min is preferable.

Cone calorimeter data, given in Table III, shows that CaSiEBA produced at the two-roll mill (CaSiEBA-10 min and CaSiEBA-20 min) has a longer ignition time and lower maximum and average heat release rates when mixed for longer times. As the commercial processing should give a more intense mixing, one would expect CaSiEBA-com to have even better flame retardant properties. It, however, shows a value in between the two others, although the values in most cases are closer to the CaSiEBA-20 min sample.

Microscopy

The analyzed samples consist of four components, i.e., chalk, silicone elastomer, EBA, and LDPE. According

to literature, binary blends of metallocene linear LDPE and ethylene/vinyl acetate copolymer with acrylate content up to 14 wt % was miscible.¹² Also, blends of acrylate acid-ethylene copolymer and LDPE have shown to be miscible at all proportions for acid contents below 5 mol %.¹³ Therefore, it is probable to assume that EBA (with its low butyl acrylate content) and LDPE are miscible as well. Consequently, the analyzed samples consist of three components, i.e., chalk, silicone elastomer, and polymer (EBA + LDPE) matrix.

SEM and ESEM/EDX

SEM images are presented in Figures 1(a)–1(f). These images provide a general representation of the dispersion of chalk particles (bright areas). Also, the presence/absence of agglomerates can be detected in Figures 1(a)–1(c), where a lower magnification was used. The mean particle size of the chalk particles is 1.4 μm , and particles with size between 5 and 8 μm are within the particle size distribution. No features above 10 μm are observed in either of the figures. The conclusion is that there are hardly any agglomerates in the analyzed samples. Also, only small effects due to the difference in mixing conditions are seen at this low magnification.

Figures 2(a)–2(c) shows the topography of gold-coated fractured surfaces, and it is seen that CaSiEBA-4 min has a rough surface, while CaSiEBA-20 min, and especially CaSiEBA-com, have smoother surfaces. The rough surface of CaSiEBA-4 min together with an indistinct location of the chalk particles indicates poor contact between the polymer matrix and the chalk particles. The adhesion between the polymer matrix and the chalk particles seems to gradually increase with longer/tougher mixing conditions, since the surfaces of CaSiEBA-20 min and CaSiEBA-com become increasingly smooth. The fracture occurs where the material is weakest, which seems to be between the polymer matrix and the border of the chalk particles. Furthermore, in CaSiEBA-20 min, chalk particles and holes in which chalk particles have most likely been located before the fracture, are seen. The chalk particles in CaSiEBA-com are well

TABLE III
Cone Calorimeter Data

Material	Max HRR (kW/m ²)	Average HRR (kW/m ²)	Average ignition time (s)	Average burning time (s)
CaSiEBA-10 min	384	264	109	314
CaSiEBA-20 min	326	194	148	414
CaSiEBA-com	364	226	139	371

HRR, heat release rates.

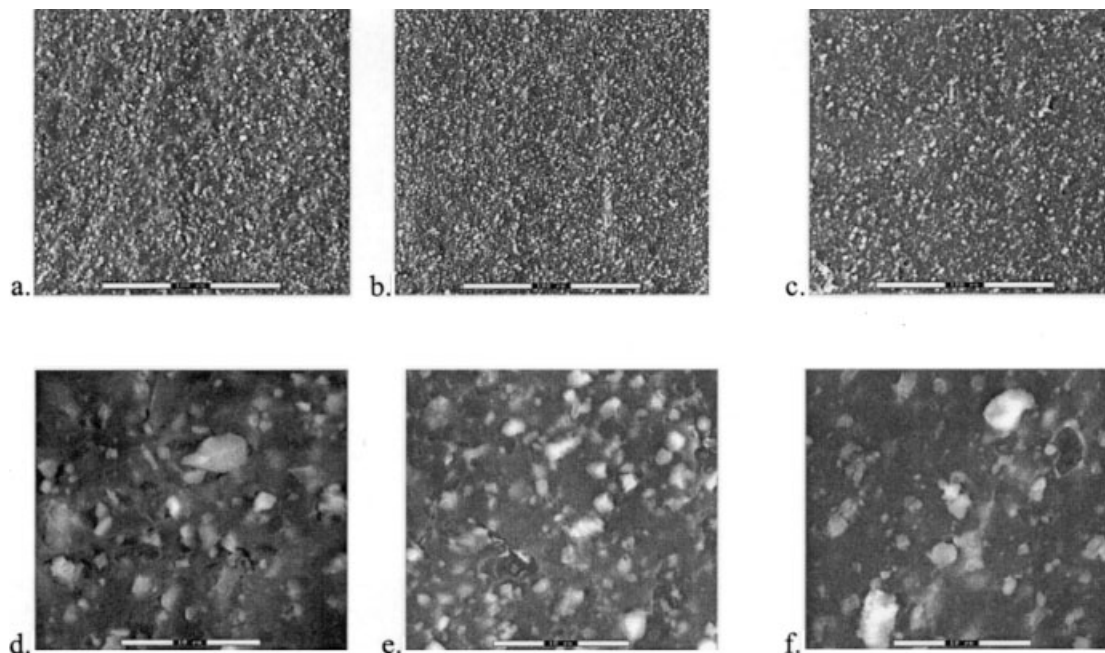


Figure 1 SE images of microtome-cut samples of CaSiEBA-4 min (a) and (d), CaSiEBA-20 min (b) and (e), and CaSiEBA-com (c) and (f) analyzed with ESEM. The magnification is $\times 500$ for (a)–(c) and the bar represents $100\ \mu\text{m}$, whereas the magnification is $\times 4000$ for (d)–(f) and the bar represents $10\ \mu\text{m}$.

embedded in the matrix, as the number of holes is significantly less than in CaSiEBA-20 min. (The rough surface of CaSiEBA-4 min and suggested poor contact between the continuous bulk polymer phase (i.e., EBA + LDPE) and the chalk particles will be verified by TEM/EDX analysis presented later on.

The presence and location of silicone elastomer cannot be visually detected in the kinds of images that are shown in Figures 1 and 2. Chemical information was instead provided by EDX. The X-ray detector provides information about where Ca and Si are present in the material (on a microscopic scale) and was used to provide elemental maps and line scans of the three compounds.

Several line scans probing for calcium atoms and silicon atoms were made on CaSiEBA-4 min,

CaSiEBA-20 min, and CaSiEBA-com. Representative scans are shown in Figures 3–5, where the intensity of calcium (originating from chalk particles) and silicon (originating from silicone elastomer) is presented as curves. Line scans of $10\ \mu\text{m}$ were typically made, and information was collected from the whole thickness of the test specimen ($0.2\ \mu\text{m}$). For the three materials, the silicon peaks generally follow the calcium peaks. This means that there is a concentration of silicone elastomer around the chalk particles, which is indicated by the information collected from the whole depth of the test specimen. The silicon peak is sometimes higher at one or both sides of the chalk peak, further supporting the enrichment of silicone elastomer around the chalk particles. The intensity of the silicon peak, i.e., the difference in the height of the peak, differs between the

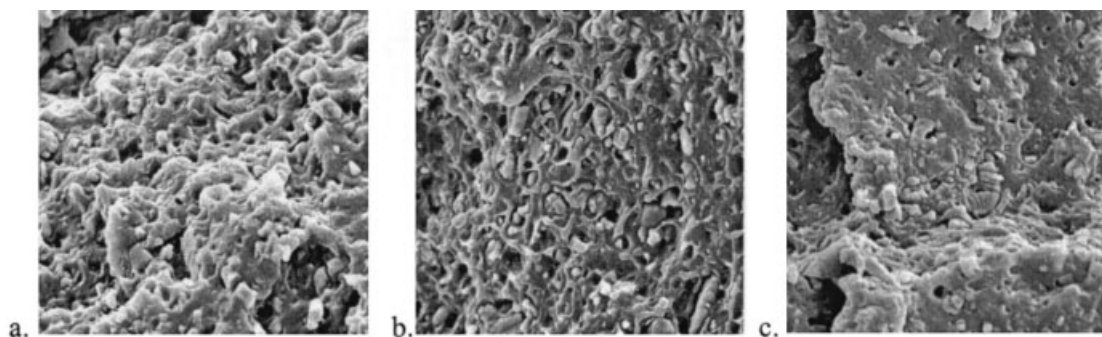


Figure 2 SE images of gold-coated fractured surfaces of CaSiEBA-4 min (a), CaSiEBA-20 min (b), and CaSiEBA-com (c) analyzed with SEM. The magnification is $\times 3000$.

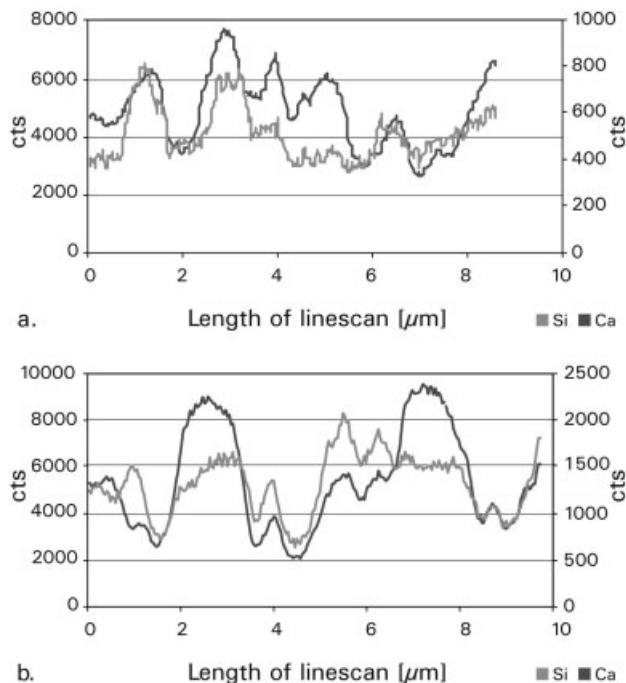


Figure 3 Line scans of CaSiEBA-4 min obtained from ESEM/EDX. The black line (left axis) represents calcium, and the grey line (right axis) represents silicone.

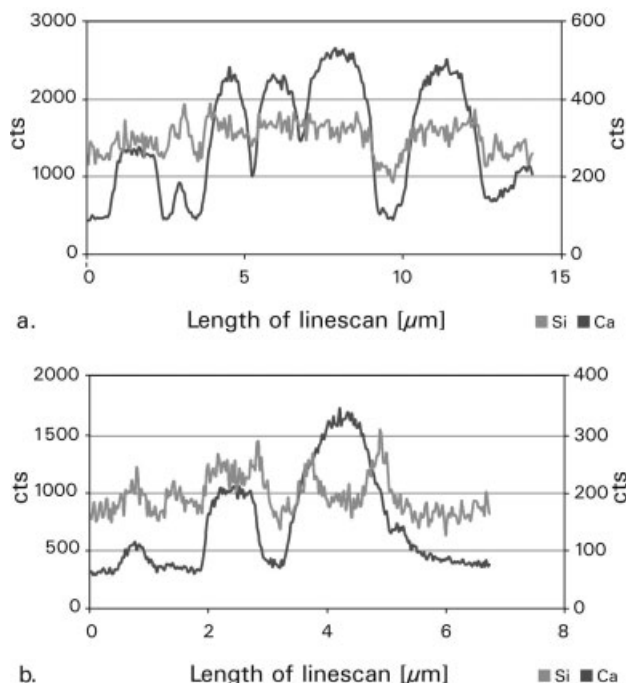


Figure 5 Line scans of CaSiEBA-com obtained from ESEM/EDX. The black line (left axis) represents calcium, and the grey line (right axis) represents silicone.

materials. The difference in peak height is large in CaSiEBA-4 min and is less pronounced in CaSiEBA-20 min. The silicon peaks in CaSiEBA-com are low, giving

an almost smooth curve with little difference between maximum and minimum peak height. A small difference in peak height (as is the case in CaSiEBA-com) indicates that the silicone elastomer is present in similar amounts in the polymer matrix and around the chalk particles, i.e., the silicone elastomer is more homogeneously dispersed in the material. Similarly, a larger difference in peak height (as in CaSiEBA-4 min) indicates a less homogeneous dispersion, where a higher enrichment of silicone elastomer is found around the chalk particles than in the polymer matrix.

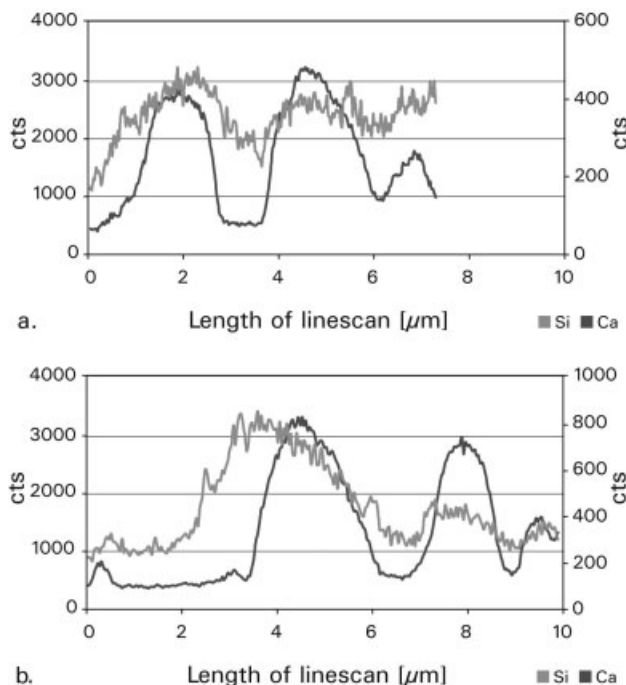


Figure 4 Line scans of CaSiEBA-20 min obtained from ESEM/EDX. The black line (left axis) represents calcium, and the grey line (right axis) represents silicone.

The peaks, i.e., the intensity of calcium and silicon, depend on the “preparation” of the test specimen. Since the chalk particles (1.4 μm) are larger than the thickness of the analyzed slice (0.2 μm), most chalk particles go completely through the slice. Fragments of chalk particles can also be present in the slice regardless of whether they are small particles or the remains of a particle that has been cut. These scenarios are schematically shown in Figure 6. Although the

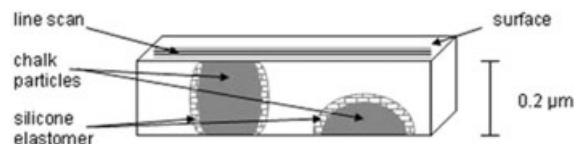


Figure 6 Possible locations (schematically and not made to scale) of chalk particles (dark grey) and silicone elastomer (white/grey checked) in the polymer matrix of CaSiEBA.

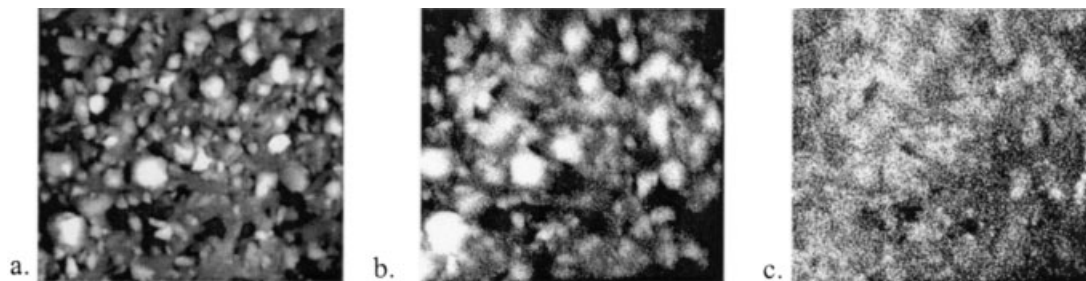


Figure 7 ESEM/EDX mapping of CaSiEBA-4 min. SE image (a), elemental map of Ca atoms (b), and elemental map of Si atoms (c). The magnification is $\times 4000$.

information provided from a line scan is collected from the whole depth of a test specimen, the preparation affects the relative intensity of the two elements (Ca and Si). The preparation makes the analysis more difficult and not as straightforward as first believed, as it affects the interpretation of the line scans. The same reasoning applies for mapping information.

Images obtained after mapping for Si and Ca are most informative when it comes to locating silicone elastomer within the polymer matrix as chalk is fairly easily detected visually (as shown in previous figures). Figure 7 shows the mapping results for CaSiEBA-4 min. The Si image is similar to the Ca image, i.e., silicon is mainly enriched at the chalk particles. A correlation between the Ca image and Si image is seen for CaSiEBA-20 min (Fig. 8) and CaSiEBA-com (Fig. 9), but is less well correlated than in the case of CaSiEBA-4 min. Further, the silicon is distributed more evenly in the polymer matrix of CaSiEBA-20 min and CaSiEBA-com, with less enrichment around the chalk particles. The silicone elastomer seems to be most homogeneously distributed in CaSiEBA-com. However, the difference depends on the intensity of the elements, which in turn depends on how many frames were added to achieve a good mapping image. In this ESEM/EDX study, frames were collected until the image started to drift, i.e., over ~ 1 h.

TEM/EDX

As in the ESEM analysis, an EDX is needed to get information from TEM analysis on the location of the

silicone elastomer. In contrast to ESEM, line scans from TEM are obtained at a higher magnification, making the information more detailed, and the information is more exact, since the electron beam is narrower in TEM. Furthermore, due to the transmitting light, it is possible to visually see through the test specimen and determine, for instance, whether the Ca intensity originates from one chalk particle or from several chalk fragments. All these factors facilitate the interpretation of the images and information from the line scans with respect to the location of both chalk particles and silicone elastomer. CaSiEBA-4 min and CaSiEBA-com were analyzed by TEM/EDX, as they have the greatest difference in manufacturing conditions (and also as they have the greatest difference in dispersion according to previous SEM and ESEM results).

Note that the line scans obtained with TEM/EDX do not provide information on the number of atoms present. It simply provides the aspect ratio between Ca and Si. As a consequence, an area that according to mapping has a low intensity of Ca can in a line scan appear to have a high concentration, which is incorrect. This is in complete contrast to the line scans obtained with SEM/EDX, which do provide information related to the number of atoms present.

A difference in the dispersion of chalk particles can be seen in Figures 10(a) and 10(b), which represent TEM images of CaSiEBA-4 min and CaSiEBA-com, respectively. (Chalk particles represent the darker areas.) The chalk particles in CaSiEBA-com are more thoroughly distributed. It is also seen that CaSiEBA-4

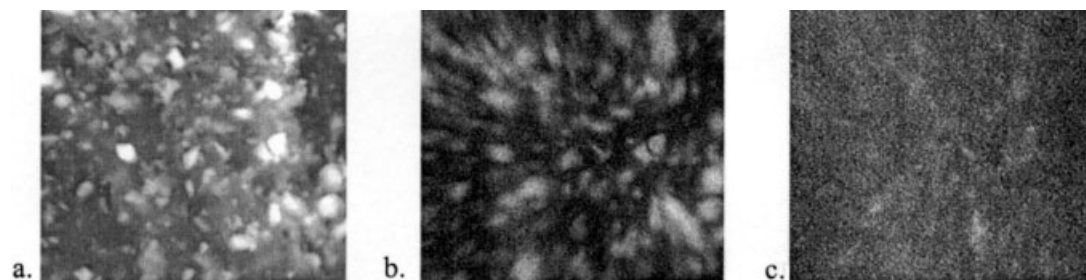


Figure 8 ESEM/EDX mapping of CaSiEBA-20 min. SE image (a), elemental map of Ca atoms (b), and elemental map of Si atoms (c). The magnification is $\times 4000$.

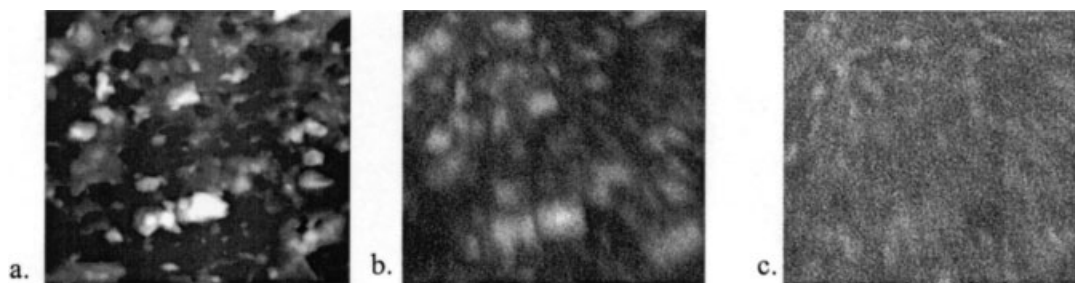


Figure 9 ESEM/EDX mapping of CaSiEBA-com. SE image (a), elemental map of Ca atoms (b), and elemental map of Si atoms (c). The magnification is $\times 4000$.

min (Fig. 10(a)) contains large areas with no chalk particles. These areas were easily etched by the electron gun (using higher voltage), demonstrating that they consisted of polymer and/or silicone elastomer. (However, the amount of silicone elastomer is only 5 wt % in comparison with 64.8 wt % polymer (EBA and LDPE)).

Mapping images of CaSiEBA-4 min and CaSiEBA-com (Figs. 11(a) and 12(a)) support the difference in dispersion seen in Figures 10(a)–10(b). The mapping images of CaSiEBA-4 min confirm that the areas that were visually judged to be chalk-free (as in Fig. 10(a)) were indeed chalk-free. They were also free of silicone elastomer, as the mapping did not detect any silicon in these areas. (Since mapping only represents one small area in the test specimen, some silicone elastomer may, nevertheless, be present in the larger chalk-free areas.) Further, mapping images show that silicon and calcium are associated with each other, i.e., silicone elastomer is concentrated around the chalk particles. This is seen in both CaSiEBA-4 min and CaSiEBA-com, but there seems to be less silicon enrichment in CaSiEBA-com, as the concentration is less distinct. For the same reason, silicon seems to be more evenly distributed throughout the polymer matrix of CaSiEBA-com. Some areas containing only silicon

were detected in CaSiEBA-4 min (see the representative area in Fig. 11(c); in the middle on the right side), but not in CaSiEBA-com.

Line scans from TEM were used to study the distribution of silicone elastomer in more detail. A line scan of CaSiEBA-4 min that starts in the vicinity of a single, isolated chalk particle and ends within the chalk particle shows that silicon is concentrated around the chalk particle (see line scan X in Figs. 13 and 14(a)). A line scan over an area containing smaller chalk particles as well as the polymer matrix (line scan Y in Figs. 13 and 14(b)) also shows that silicon is concentrated around the chalk particles and is present in the polymer matrix as well.

Figures 15(a)–15(b) show TEM/EDX line scans of CaSiEBA-com. The line scan shown in Figure 15(a) starts in the near vicinity of a single, isolated chalk particle and ends within the particle. The line scan shows an enrichment of silicon at the boundaries of the chalk particle (similar as for CaSiEBA-4 min). In a line scan over an area containing smaller chalk particles distributed in the polymer matrix, it is seen that the silicon signal increases when the calcium signal decreases and *vice versa* (Fig. 15(b)). Further, when the chalk signal is at its half intensity (half of its maximal height), the silicon signal is also at its half intensity,

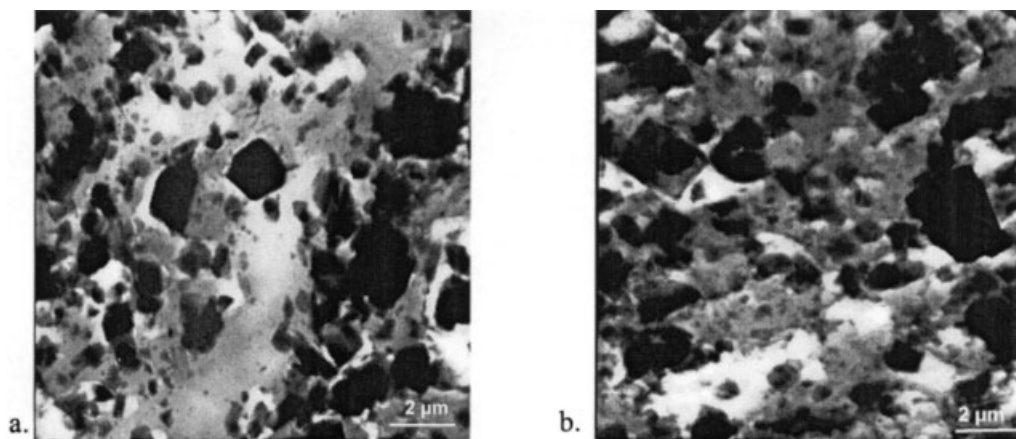


Figure 10 SE image of CaSiEBA-4 min (a) and CaSiEBA-com (b) obtained by TEM. The bar represents 2.0 μm .

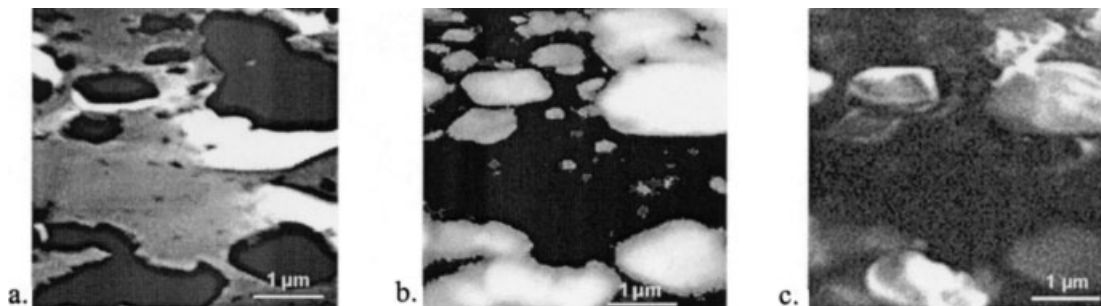


Figure 11 TEM/EDX mapping of CaSiEBA-4 min. Bright-field image (a), elemental map of Ca atoms (b), and elemental map of Si atoms (c).

indicating a homogeneous dispersion of silicon in the matrix of CaSiEBA-com.

TEM/EDX line scans of CaSiEBA-4 min and CaSiEBA-com (Figs. 16(a) and 16(b)) were also done in areas that according to mapping contained no or very low amounts of calcium. The line scans showed that chalk particles, or more likely fragments of chalk particles, was present in the polymer matrix of both materials. Silicon was also present in both matrices, but the curves (intensity) of Ca and Si are smoother in CaSiEBA-com than in CaSiEBA-4 min, where they fluctuate to a great extent. The fluctuation means that the concentration of Ca and Si within that area is low and further indicates that the amount of both chalk fragments and silicon elastomer are higher and more homogeneously distributed in the polymer matrix of CaSiEBA-com.

DISCUSSION

Previous studies on the flame retardant mechanism of CaSiEBA formulations, including the effect of each component, show that the addition of chalk and silicone elastomer is important for obtaining good flame retardant properties.¹¹ The flame retardant effects of chalk and silicone elastomer are briefly explained further to afford a better understanding of the discussion that follows. For interested readers a more detailed

discussion and relevant references are found in Ref. 11.

The main effects of chalk are the following:

- Dilution: 30 wt % of combustible polymeric material is replaced with inert filler.
- Postponing the degradation of EBA: The major mass loss of EBA occurs at 425°C (with chalk), instead of at 350°C (without chalk).
- Formation of ionomer: Ionomers are formed between carboxylic acid (after ester pyrolysis of EBA) and calcium ions in the chalk. The ionomers act as crosslinks, increasing the viscosity.
- Stabilization of the silicone elastomer/postponing the degradation of the silicone elastomer: The chalk neutralizes acidic residues left in the silicone elastomer from its polymerization process. Hence, the silicone elastomer degrades at higher temperatures.

The main effect of the silicone elastomer is the formation of SiO₂. It is shown that the creation of a stable surface layer is important for the flame retardant properties of CaSiEBA. The silicone elastomer degrades to low molecular oligomers (when the temperature is between 300 and 350°C) and migrates to the air-polymer interface, where it is oxidized to SiO₂. No SiO₂ is formed in the bulk as the temperature¹⁴ as well

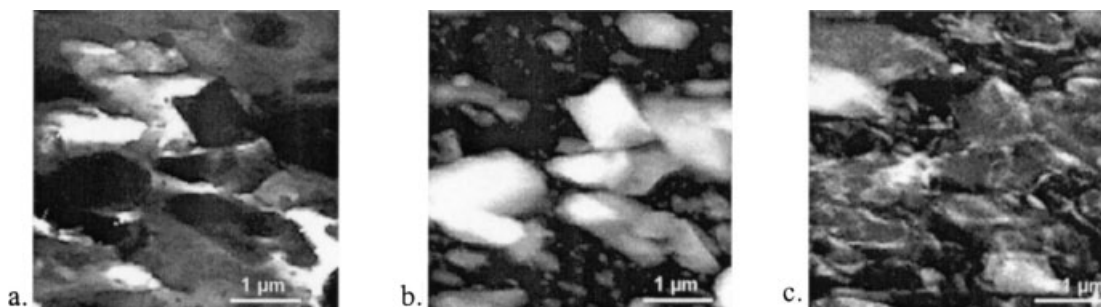


Figure 12 TEM/EDX mapping of CaSiEBA-com. Bright-field image (a), elemental map of Ca atoms (b), and elemental map of Si atoms (c).

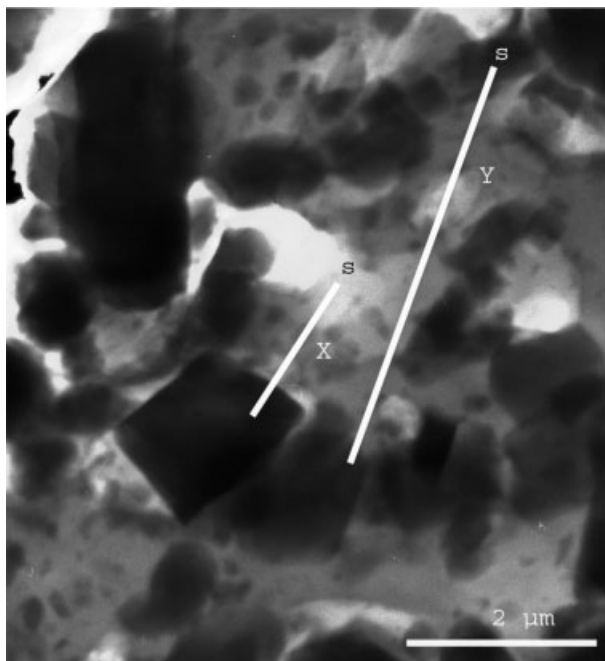


Figure 13 TEM SE image of CaSiEBA-4 min including line scan X and Y. S indicates the start position of the line scan.

as the oxygen concentration is too low there. The SiO₂ is believed to form a protective layer that contributes to the reduction of burning of the underlying material.¹⁵ (At temperatures above 700°C, SiO₂ reacts with

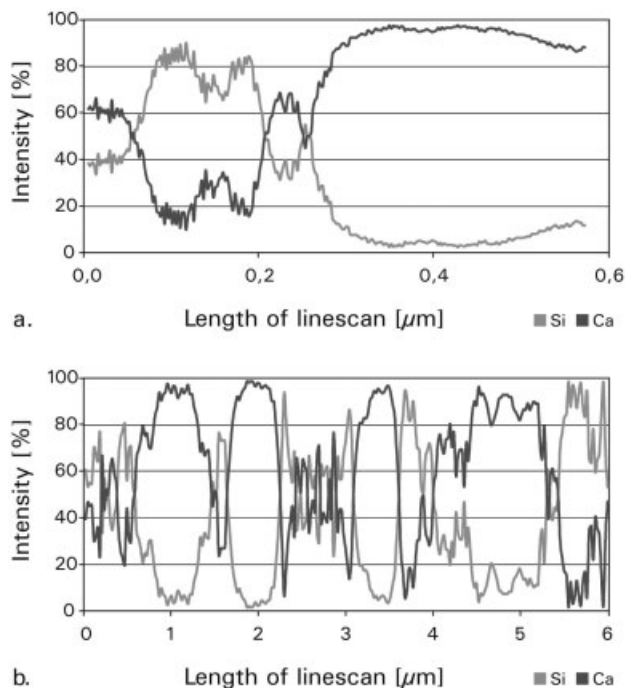


Figure 15 Line scans of CaSiEBA-com obtained from TEM/EDX. Line scan near and into one chalk particle (a) and line scan over the matrix (b). The black line represents calcium, and the grey line represents silicone.

CaO (degradation product of calcium carbonate) and forms calcium silicate. This is, however, a secondary effect and will not be discussed further.)

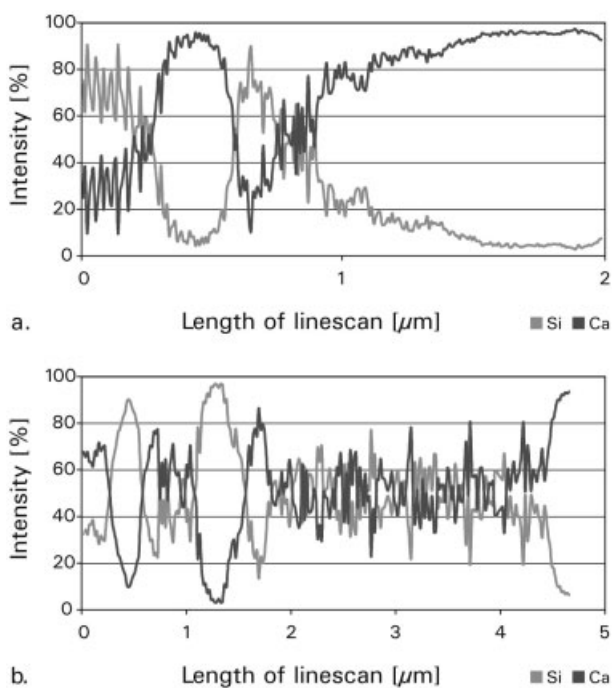


Figure 14 Line scans of CaSiEBA-4 min obtained from TEM/EDX. (a) and (b) represent line scans X and Y given in Figure 13, respectively. The black line represents calcium, and the grey line represents silicone.

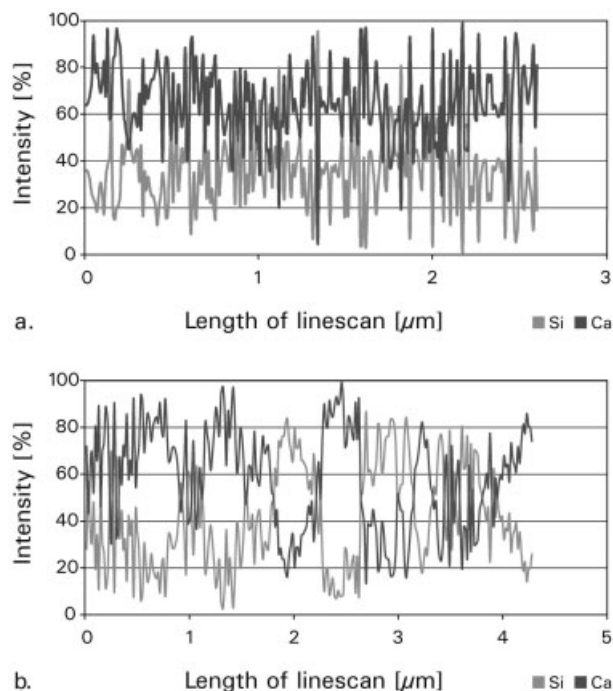


Figure 16 TEM/EDX line scans in the matrix of CaSiEBA-4 min (a) and CaSiEBA-com (b). The black line represents calcium, and the grey line represents silicone.

All the above effects are important to the flame retardancy, but postponement of the degradation of EBA, ionomer formation, stabilization of the silicone elastomer, and formation of a SiO₂ enriched surface layer are especially believed to depend on the degree of dispersion of both chalk particles and silicone elastomer. Dilution with 30 wt % chalk gives solely a volume effect, whereas the others are affected by interactions between the solid phase and the melt phase and ought to be improved by a more homogeneous dispersion.

It is seen that the fire retardant properties of CaSiEBA are improved when the material has been subjected to more extensive mixing. According to microscopy results, dispersion of chalk particles and silicone elastomer correlates with mixing conditions. Figures 1(a)–1(c) showed that the dispersion of chalk particles was improved with extensive mixing. This is most likely a result of improved contact/adhesion between chalk particles and the polymer matrix. Figures 2(a)–2(c) indicates this, as the surface fracture goes from rough to smooth with more extensive mixing. A homogeneous distribution of chalk particles in the polymer matrix probably enhances the contact area between the polymer and the chalk particles. This is of importance to both ionomer formation and the postponement of the degradation of polymer. Well-dispersed chalk particles provide more particle area, i.e., a greater area is available for contact and, consequently, facilitates reaction between the carboxylic acid groups in the polymer chain and the calcium ions in the chalk, which most likely, then, promotes the formation of ionomers. The formation of ionomers is important to the melt stability, as ionomers increase the stability of the (initial) melt through crosslinks. Further, chalk postpones the degradation of the polymer, as seen in thermal gravimetric analysis.¹¹ This is most likely a result of the increased diffusion path brought about by well-dispersed chalk particles. The volatile low-molecular gases formed during degradation have a longer path to the surface of the specimen, i.e., the escape of gases takes a longer time.

CaSiEBA forms a surface layer simultaneously with ignition of the material. (This is clearly seen in cone calorimeter tests.¹⁴) The surface layer has several effects. For instance, it provides insulative properties that hinder the heat of the flame from reaching the bulk, hence, postponing the degradation of the material in the bulk. Further, it slows down the evaporation of volatile gases. Hence, the gases ignite later and the fire behavior is less intense. As said earlier in the discussion, the initially formed surface layer consists of SiO₂ because of the reaction between silicone elastomer and oxygen at the polymer/air interface. Pure silicone elastomer degrades when subjected to ~300°C. When chalk is present, however, as in CaSiEBA, the main degradation temperature of sili-

cone elastomer increases by ~150°C.⁹ Chalk has a positive effect on silicone elastomer, because chalk neutralizes acidic residues present in the silicone elastomer from its polymerization process, residues that otherwise are destructive for the silicone elastomer. Microscopy results (line scans shown in Figs. 3–5) showed that silicone elastomer was enriched around the chalk particles in all three materials, although the degree of enrichment differed between the samples. More extensive mixing led to a less obvious enrichment around the chalk particles and a more homogeneously dispersed silicone elastomer in the polymer matrix. (This was seen when comparing Fig. 11(c) (CaSiEBA-4 min) with Fig. 12(c) (CaSiEBA-com).) The neutralization of the acidic residues in CaSiEBA-4 min, CaSiEBA-20 min, and CaSiEBA-com is similar; however, since all samples were subjected to similar mixing at the initial stages (the beginning) of the compounding process. If the acidic residues are not neutralized, i.e., residues are left in the material, the silicone elastomer will start to depolymerize in the bulk at temperature as low as 300°C and formation of SiO₂ at the surface will not take place.

The difference in silicone elastomer enrichment was also seen in Figures 2(a)–2(c), where a lower cohesive strength between the silicone elastomer and the polymer matrix is believed to be responsible for the rough surface fracture of CaSiEBA-4 min. The surface fracture of CaSiEBA mixed more toughly and for longer times, i.e., CaSiEBA-20 min and CaSiEBA-com, is smoother and indicates a more homogeneous dispersion of silicone elastomer. Homogeneous dispersion of silicone elastomer is important, as it facilitates an even formation, i.e., a uniform thickness, of SiO₂ at the surface. This will improve the surface's ability to withstand the pressure of volatile gases formed in the bulk, and the initial crack propagation that occurs at the weakest spots (lowest thickness) can most likely be reduced or perhaps entirely avoided. Furthermore, in terms of crack propagation in the surface char, it is important that the surface layer forms instantly over the whole surface. This is also facilitated by a homogeneous distribution of silicone elastomer in the polymer matrix.

CONCLUSIONS

Both ESEM/EDX and TEM/EDX have proven to be useful techniques for obtaining information on the dispersion of chalk particles and silicone elastomer in the halogen-free flame retardant system analyzed here. The chalk particles are rather easily detected (visually) at a certain magnification, and X-ray information enhances the information on chalk particles and provides information on the presence of the silicone elastomer. A combination of SEM, ESEM/EDX,

and TEM/EDX was needed to come to the conclusions presented in this study.

More extensive mixing provides a better dispersion of both chalk particles and silicone elastomer, as well as improved flame retardant properties. Several mechanisms behind the flame retardancy are affected by reactions/interactions between phases or transactions over phases. It is, thus, of vital importance to know the effect of dispersion and how it can be improved. More extensive mixing leads to a larger contact area between the chalk particles and the polymer matrix, which is positive for the interactions and the chemical mechanisms occurring between the solid phase and the melt phase. A well-dispersed silicone elastomer most likely has a positive effect on char formation, where it affects both the homogeneity of the protective surface layer and the initial crack propagation in the surface layer.

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