is a small number of the order of 10^{-1}. The relative energy contribution on the basis of eq 19 and 20 is

$$\frac{f_e}{f} = 1 - \frac{\mathrm{d}\ln G}{\mathrm{d}\ln T} - \frac{\beta T}{3} + \gamma\beta T \qquad (21)$$

which differs from eq 6 by the term $\gamma\beta T$. If γ were 0.1, then for natural rubber at room temperature ($T = 300°\mathrm{K}$, $\beta = 6.6 \times 10^{-4}\ \mathrm{deg}^{-1}$) $\gamma\beta T = 0.02$. However, there is at present as yet insufficient data to establish unequivocally the nonzero nature of the γ parameter. Thus within the framework of the current statistical theory ($\gamma = 0$), shear modulus is independent of the application of hydrostatic pressure.

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Effect of Fillers on the Photooxidative Stabilization of Polyethylene

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ABSTRACT: The influence of fillers on the morphology of the polymer matrix is shown to be as important as light shielding in the photooxidative stabilization of polyethylene. High surface energy fillers (*i.e.*, diamond and graphite) which generate a highly structured polymer matrix and are effective light shields enhance the photodegradative process. Low surface energy fillers (*i.e.*, polytetrafluoroethylene and polychlorotrifluoroethylene) which are not effective light shields and do not influence the morphology of the matrix are moderately effective photostabilizers. It is proposed that the stabilization of the carbon black filled polyethylene is due not only to its light shielding capability but also to its moderately low surface energy. Our experiments indicate that light shielding in combination with a low surface energy filler promote protection to photooxidative degradation.

The photooxidative protection of polyethylene afforded by fillers, such as carbon black, is believed to be due to its light shielding properties and, in some cases, to its action as a synergistic agent for the antioxidant.[1] However, it is recognized that fillers have a considerable influence on the morphology and physical properties of the polymer in a polymer–filler composite.[2,3] In this paper, we shall demonstrate the effect of fillers on the morphology of polyethylene matrices and how this, in turn, contributes to the photooxidation resistance of the polymer. This effect has not been studied to any extent.

Previous studies[4] have shown that thin polyethylene films (1 mil), when nucleated and crystallized in contact with a high surface energy substrate, produce a transcrystalline region in the polymer which differs in both morphology and mechanical properties from that found in the normal spherulitic structure. Since one of the controlling factors in the oxidative stability of polyethylene is related to its morphology,[1] it was believed probable that the photooxidative resistance of a "polyethylene-plus-filler" composite may be affected by the nature of the filler surface.

To investigate this possibility, we exposed a series of polyethylene films containing different types of high and low surface energy fillers to photooxidative conditions and followed the oxidation process in each film by infrared spectroscopy. We report here the results of that study.

Experimental Section

A low density (0.919 g/cc) finely powdered polyethylene containing no antioxidants and identified as DKPC (Union Carbide Co.) was used throughout this study. A series of "PE + filler" samples was prepared containing 3% (w/w) of the following powdered fillers: carbon black (Kosmos BB), polychlorotrifluoroethylene (CTFE), polytetrafluoroethylene (PTFE), KBr, diamond, and graphite. The choice of filler was governed by surface free energy considerations which are related to the nucleating ability of the filler material. Table I lists the various fillers and pertinent data.

TABLE I
SURFACE AND BULK PROPERTIES OF FILLERS

Filler	Density (ρ), g/cm^3	Particle size	Surface free energy, ergs/cm^2
Diamond	3.51	0.5–1.0 μ	>1000[a]
Potassium bromide	2.1	<0.1 μ	~200[b]
Graphite	2.2	<0.1 μ	~110[c]
Carbon black	1.9	180 Å	~50[c]
Polychlorotrifluoroethylene	2.1	<0.1 μ	31[d]
Polytetrafluoroethylene	2.2	<0.1 μ	18.5[d]

[a] Calculated from B. V. Belogurov, *Russ. J. Phys. Chem.*, **34,** 206 (1960). [b] Extrapolated melt surface tension. [c] Estimated from heat of wetting and wettability: A. C. Zettylmoyer, *J. Colloid Interfac. Sci.*, **28,** 343 (1968). [d] Critical surface tension of wetting.

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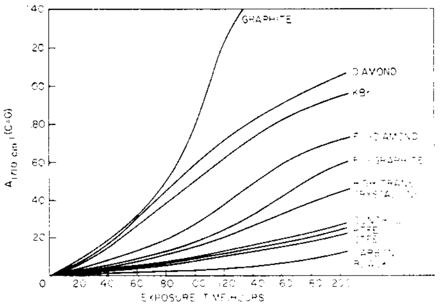

Figure 1. Rate of photooxidation of 1-mil polyethylene films containing 3% (w/w) of various fillers.

Each "PE + filler" sample was mixed thoroughly and then molded at 200° into 1-mil films between sheets of PTFE. Each sandwich-like assembly containing the "PE + filler" film was placed in an oven at 210° for 45 min in a positive nitrogen atmosphere. This treatment allows ample time and temperature to ensure extensive molecular contact between the filler surface and the molten polyethylene.[5] The sandwich-like assemblies were cooled to room temperature in nitrogen and removed. The "PE + filler" films were exposed simultaneously in a cell[6] which had a quartz window and was provided with a means of passing pure oxygen over the samples while exposed to an RS-Sunlamp (GE), 5 in. from the samples. The cell was partially immersed in a constant-temperature bath (20°) to avoid possible thermal oxidation effects.

The infrared spectra were recorded on a Model 421 Perkin-Elmer spectrophotometer and the ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The heats of fusion of the polymer–filler composites were recorded with a Perkin-Elmer DSC 1B.

Results and Discussion

In Figure 1, the absorbance of the carbonyl absorption at 1710 cm^{-1} (used as a measure of oxidation[7]) is shown as a function of exposure time for a variety of "PE + filler" samples in comparison to a control film with no filler.

Using the "control film" as a reference point, we can see that the carbon black filler provides the expected protection. We can also see that the low surface energy fillers, such as PTFE and CTFE, also provide some degree of protection. However, in direct contrast, the high surface energy fillers such as graphite, diamond, and KBr actually enhance the photooxidative degradation of the films on exposure to simulated sunlight.

In Figure 2, the uv and visible (220–700 mμ) transmission spectra of the various "PE + filler" films show the relative light shielding effect of the fillers in the films. All the "PE + high-surface energy filler" films transmit approximately the same amount (~5% transmittance) of the strongly degrading uv radiation (*i.e.*, 260–280 mμ). In particular, the "PE + carbon black" and the "PE + graphite" films transmit virtually the same amount of radiation while the "PE + diamond" is an even more effective light shield; yet the graphite and diamond filled films are more severely photooxidized than the carbon black filled film (Figure 1) after exposure.

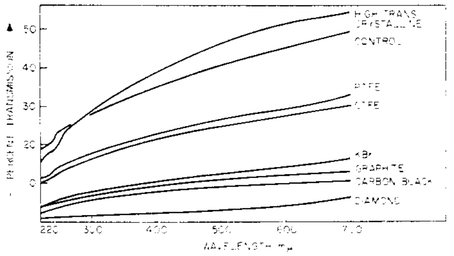

Figure 2. Per cent transmission of 1-mil polyethylene films containing 3% (w/w) of various fillers.

This evidence shows that although light shielding is of considerable importance, other factors related to the filler surface should be considered.

Microscopic examination of the polyethylene nucleated in contact with high surface energy fillers such as diamond, graphite, and KBr revealed a highly structured transcrystalline region[8–11] localized around the filler particle. Numerous crystallization nuclei were formed at the polymer–filler interface; the spherulites which grew from the nuclei propagated in only one principal direction, since growth in the lateral directions is inhibited by neighboring spherulites. In this way, only very narrowly divergent spherulite sectors developed, which gave the transcrystalline region a rodlike appearance. However, when polyethylene was nucleated on the relatively low surface energy carbon black, the transcrystalline region, while present, was minimized. There was no transcrystalline region generated in the polymer matrix when nucleated on CTFE or PTFE. Although the samples differed in their extent of transcrystalline region, the crystallinity of the samples, as measured by heat of fusion, showed no essential differences ($\Delta H_f = 21 \pm 1$ cal/g).

It appears that the presence of a highly structured region at the polymer–filler interface such as we have in the graphite, diamond, and potassium bromide filled films has a deleterious effect on the photooxidative stability of the polymer–filler composite. However, light shielding and a negligible amount of transcrystalline region (as found in the carbon black filled polyethylene film) apparently is effective in producing a composite which is more stable to photooxidative degradation. Fillers, such as CTFE and PTFE, which are ineffective light shields (Figure 2), but which prevent the formation of a transcrystalline region in the polyethylene, are moderately effective in their stabilizing properties (Figure 1). Thus, light shielding as well as the presence of a low surface free energy filler apparently contribute to the photooxidative stability of a "PE + filler" film.

In order to show that a transcrystalline PE film without filler was actually more susceptible to photooxidation than the control, we exposed a film which was generated in contact with an evaporated gold film and known to be entirely in the transcrystalline form.[12] This film contained no filler and it differed from the control only in morphology. In Figure 1, it can be

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seen that the rate of degradation in the transcrystalline film (no filler) is in fact more rapid than in the control. These results then indicate that in order to improve the photooxidative stability of polyethylene, a filler, in addition to being a light shield, should preferably have a low surface energy.

To further support this hypothesis, the high surface energy fillers, graphite and diamond, which originally contributed to a high rate of photooxidation on exposure (Figure 1) were converted into low surface energy materials by direct fluorination with fluorine gas for 1 hr at ambient conditions. Since polymers have been known to convert their surface layers into perfluorinated species,[13] the increase in hydrophobicity of the diamond and graphite is believed to result from partial fluorination of their respective surfaces.

In Figure 1, comparison of the PE films containing the fluorinated graphite and fluorinated diamond with the original "PE + graphite" and "PE + diamond" films reveals the increased protection afforded by the now lower surface energy graphite and diamond fillers. The observed increase in protection to photooxidation is believed to result from a combination of light shielding and a decrease in the highly structured region around the filler particles.

The results of Eby[10] support the hypothesis that a layer of lamellar oriented normal to the surface augments diffusion into the polymer. Eby obtained a value of 3.6×10^{-8} cm^2 sec for the diffusion constant of ethane into a transcrystalline region and a value of 1.7×10^{-8} cm^2 sec for the bulk (spherically symmetrical spherulites). Michaels and Bixler[14] have demonstrated quite clearly that diffusion of oxygen into a high density linear polyethylene is one order of magnitude greater than ethane (diffusion constant = 17.0×10^{-8} cm^2/sec) and that the diffusion is extremely sensitive to crystallinity. Michaels and Bixler[14] estimate that the diffusion constant of oxygen in amorphous polyethylene would be 173×10^{-8} cm^2/sec, or ten times that of linear high density polymer (77% crystalline). Since the boundary between neighboring spherulites is considered to be relatively amorphous,[10] it then becomes apparent why the transcrystalline regions are more susceptible to oxidative photodegradation. In the transcrystalline morphology, considerably more boundary regions exist, permitting greater access of excited oxygen[15] to the polymer resulting in the observed degradation.

It is possible that other factors may be involved in determining the polymer photooxidative stability of composites, but it appears that the influence of fillers on the morphology of the polymer matrix should be considered extremely important. A more detailed report concerning other physical and chemical effects associated with polymer–filler composites is in preparation.

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Fold Structure of Polyethylene Single Crystals

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ABSTRACT: Using model compounds we have observed infrared absorptions which can be attributed to the folding and bending conformations in *n*-hydrocarbons. Comparison of the crystalline and melt spectra of *n*-hydrocarbons and tightly folded cyclic C$_{34}$H$_{68}$ provides evidence that an absorption at 1340 cm^{-1} is associated with folding or bending in a hydrocarbon chain. Our results also corroborate the assignment of the 1350-cm^{-1} band to *gauche* conformation in *n*-hydrocarbons. Based on a comparison of the relative intensities of the 1340/1350-cm^{-1} bands in the spectrum of polyethylene single crystal aggregates it appears that the fold structure is not that of a tight fold with adjacent reentry.

Chain folding in polyethylene single crystals is an accepted phenomenon.[1] However, the nature of the fold structure, whether there is adjacent reentry,[2] switchboard-type folding,[3] a loosely looped fold model (essentially amorphous),[4] or any combination of the above, is an active area of research.[5]

Krimm and Bank[6,7] have recently concluded, based on an infrared study of the 71-cm^{-1} absorption in polyethylene single crystals consisting of a mixture of normal and deuterated hydrocarbons, that there is adjacent reentry. Okada and Mandelkern[8] report that their studies of the fold structure of polyethylene single crystals using infrared spectroscopy support the concept of a disordered surface region in the crystals that are formed from xylene. The results of Okada and Mandelkern are in accord with other measurements such as wide-angle X-ray,[9] broad-line nmr,[10] and selective oxi-

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