

NOTES

Pigment Dispersion in Thermally Modified Polyethylenes

INTRODUCTION

Among the important criteria for the economic production and marketing of filled and reinforced polymer systems are the uniform and rapid dispersion of the chosen particulate in the polymer matrix. In recently reported work,¹ we have focused attention on this problem using polyethylene (LDPE) and chlorinated polyethylene (CPE) as hosts, and a series of surface-coated rutiles as filler. Particular attention was given to the contributions made to dispersion processes by acid/base interactions between host and filler and by the state of inherent agglomeration in the particulates. It was found that, in the nonpolar LDPE matrix, the relative acidity or basicity of fillers did not contribute significantly to dispersion processes, but the dispersion parameters were influenced by the inherent state of agglomeration in the pigments. The opposite was found for the acidic CPE host: Here acid/base interactions influenced the dispersion indexes, while agglomeration states seemed not to play an important role. These findings were based on the following set of experimental criteria:

Acid / Base Interaction. Interaction parameters Ω , indicative of the relative acidity or basicity of rutiles and polymers, were obtained from inverse gas chromatographic (IGC) measurements, using *n*-butanol and butylamine as reference acid and base vapor probes. The IGC method has been described in the literature,²⁻⁴ and Ref. (1) states the various assumptions needed to generate the Ω parameter. Within the limits of these assumptions, negative Ω values denote a Lewis acid, positive Ω a Lewis base, while at $\Omega \sim 0$ the solid may be amphipatic or devoid of acid or base functionality.

Inherent Agglomeration. Principles of powder rheology⁵ were adapted to offer an index of inherent agglomeration, C . This was obtained by shearing constant volumes of dry pigment in a Brabender mixer at constant mixing speed but under varying applied loads L and recording the equilibrium torque (resistance to shearing), τ_e , offered by the powders. From theory,⁵ it followed that

$$\tau_e = CA + \mu AL \dots \quad (1)$$

where μ is an internal friction coefficient and A is an apparatus constant. Excellent linear plots of τ_e vs. L were obtained,¹ and from these followed C .

Dispersion Criteria. Constant volumes of rutile were dispersed into molten polymer hosts in a Brabender mixer operating under reference temperature and shearing conditions.¹ The apparent energy requirement, E , for attaining steady states of dispersion was computed by integrating under the torque/time curves for each rutile/host combination. In addition, dispersion quality was evaluated by intensity of segregation indexes, I ,⁶ obtained from statistical analyses of X-ray contact micrographs. This latter approach is not involved in the present communication.

The experiments of Ref. 1 involved relatively mild shearing conditions. It is possible that in more intensive shear fields the differences in dispersion behavior noted above would be reduced in importance. Nevertheless, important consequences seem to arise from the reported findings. Evidently, particulates such as rutile should not be considered as generic chemicals since their performance may depend strongly on details of surface modification applied to them. Implied in that statement is the potential ability of users to select pigments and fillers on the basis of their acid/base characteristics, with a view to optimizing selected properties of the filled polymer.

In the present note, we enlarge on the reality and the importance of interfacial phenomena in the dispersion of particulates in polymer hosts. To do this, the rutiles of Ref. 1 have been dispersed in LDPE and LLDPE resins, as received from the suppliers, and also after polarity had been introduced in the polymers by deliberately initiating thermochemical changes in them.

TABLE I
Properties of Rutile Pigments

Pigment code	Area (m ² /g)	Surface coating	Ω	C
A	7.4	None	0.06	790
B	8.5	Inorganic	1.27	590
C	7.6	Inorganic	5.25	280
D	8.9	Inorg./Org.	0.02	110
E	8.5	Inorganic	1.69	75
F	8.7	Organic	-0.42	170
G	8.6	Inorg./Org.	-0.50	5

EXPERIMENTAL

Matrix Polymers. The LDPE was a melt index 1.2 resin with a density of 0.919 g/mL, and with an M_w of 1.1×10^5 as determined by size exclusion chromatography. The LLDPE was a hexene copolymer with a melt index of 4 and $M_w = 8.2 \times 10^4$. These materials were used as received and also after samples had been exposed to 220°C by milling in a Brabender mixer at a motor speed of 50 rpm for periods up to 180 min. In preliminary work with a Perkin-Elmer DSC-2 calorimeter, it was shown that oxidative changes occurred in these polymers after some 20–25 min at this temperature.

Particulates and Dispersion. The rutiles were those involved in the work of Ref. 1. Their Ω and C values are given in Table I, along with other pertinent surface properties. The pigments have very similar BET surface areas. The surface coatings, however, produce wide differences in agglomeration and acid/base balance. Increasing C values indicate increasing inherent agglomerate strength. Pigments B, C, and E are Lewis bases, F and G are acids, and A and D are considered to be amphipatic. Dispersion experiments involved mixing the rutiles into LDPE and LLDPE melts, using the Brabender instrument at 190°C, 50 rpm motor speed. Mixing was

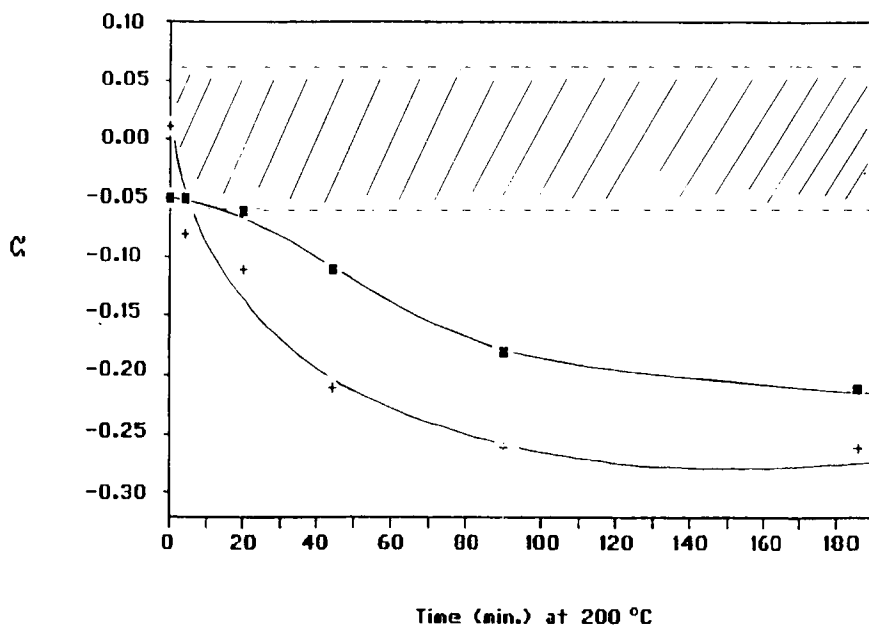


Fig. 1. Change in acid/base parameter following high T exposure of polyethylenes. Shaded part denotes amphipatic range. (■) LDPE; (+) LLDPE.

continued until a steady-state torque was obtained. The apparent energy for dispersion, E , was then calculated from the area under the torque vs. time curve, as noted above. Values of E were then used in correlations with the pigment parameters C and Ω .

Polymer Characteristics. The acid/base interaction potential of LDPE and LLDPE was measured by the IGC routines described previously.¹ Chromatographic columns containing between 8 and 11 wt % of these polymers supported on Chromosorb AW were used to obtain initial Ω values for the polymers. The columns were then exposed to 220°C for times equivalent to those used in the controlled degradation sequence described above, and Ω determinations at 30°C were repeated following each high-temperature stage. Admittedly this could only approximate the oxidative conditions prevailing during the high temperature shearing of the polymer melts. Nevertheless, useful indications may be obtained in this manner of the changes in surface acid/base properties when polyolefins begin to degrade thermally.

RESULTS AND DISCUSSION

The acid/base interaction potential of LDPE and LLDPE surfaces, and its variation with high temperature exposure time, is given in Figure 1. The initial Ω values place both polymers into the region of amphipatic or nonpolar behavior. Given the nature of polyolefines, it is concluded that surface forces are primarily dispersive, with a slight acceptor tendency displayed by LDPE. Following some 20 min exposure to 220°C, however, these polymers begin to display increasing surface acidity, the effect being more noticeable in LLDPE than in LDPE. The mechanisms of oxidative degradation in polyolefines have been understood for some time.⁷ The present results may be among the first, however, to show that the chain scission/crosslinking steps which are implicated generate strong electron acceptor characteristics in polyethylene, the more so in the linear copolymer than in the highly branched homopolymer. The effects of these surface changes on dispersion behavior of pigments are examined below.

Primary attention is focused on the apparent energy requirement for dispersion, and its variation with the Ω and C indexes of rutile pigments. Figure 2 illustrates the main findings of our inquiry, the polymer depicted being the LDPE. In the polymer as received, there is little

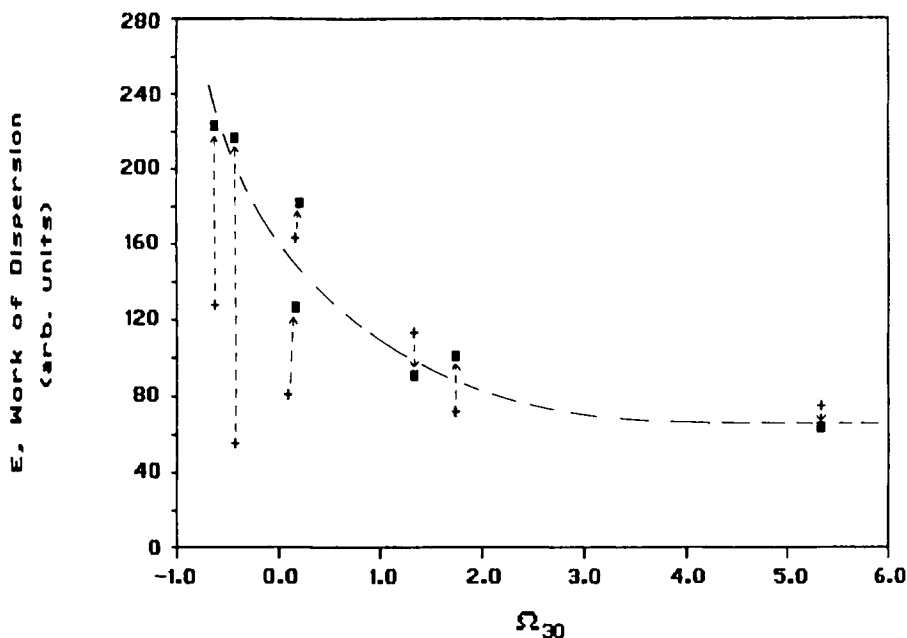


Fig. 2. Path of energy for dispersion parameter E for rutiles in LDPE in going from control to thermally degraded version of the polymer: (+) control LDPE; (■) LDPE exposed to 220°C/180 min.

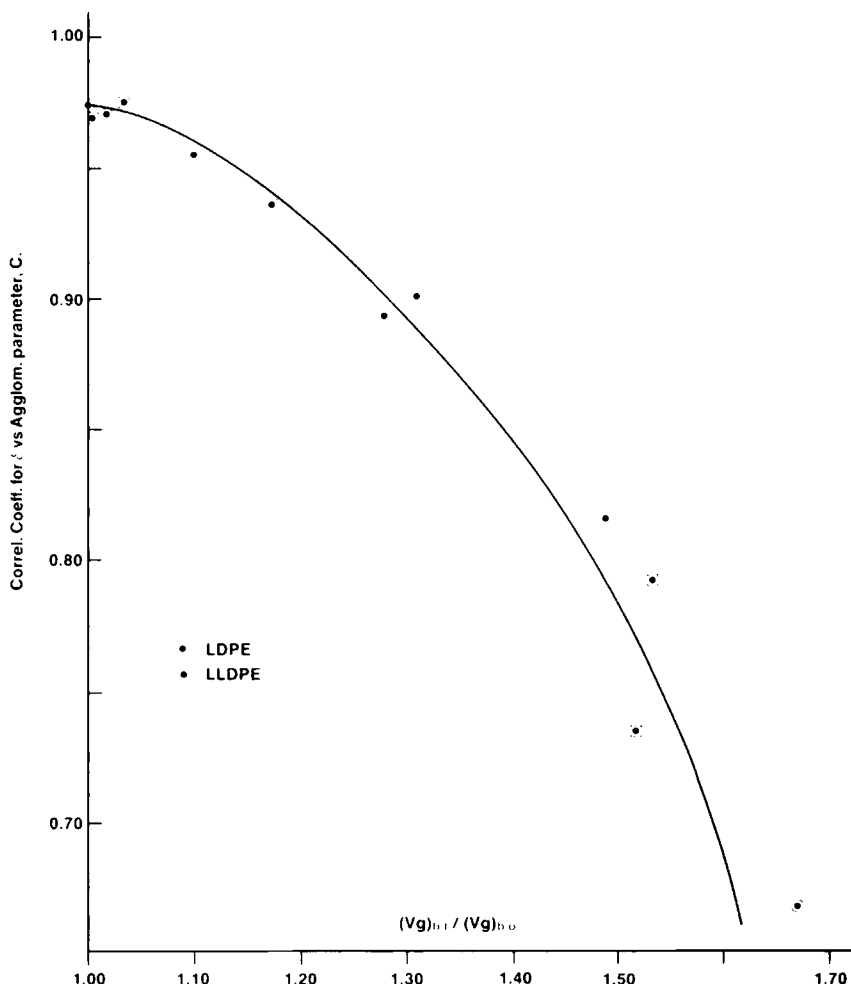


Fig. 3. Evolution of correlation coefficient for energy parameter E and pigment agglomeration parameter C with changing acid/base balance in host polymer.

relationship between E and Ω , as already discussed in Ref. 1. As the host polymer develops acid characteristics due to high temperature exposure, the correlation improves, the position of the E parameter following the paths indicated in Figure 2. Analogous findings with LLDPE attest to the generality of these trends. Furthermore, the relationship between E and the agglomeration index also shifts, but, as expected, in the opposite direction. There is strong correlation between E and C when the host polymer is used as received, and this changes to progressively weaker correlations as the polymers shift toward acid characteristics.

The correlation coefficients relating the energy parameter E for each of the polymers with each of the pigment descriptors Ω and C were computed by regression analysis. They are plotted in Figures 3 and 4 against the ratio $(V_g)_{b,t} / (V_g)_{b,0}$. This compares specific retention volumes V_g , for the basic (butyl amine) vapor probe by the polymers following time t of exposure to 220°C with the initial retention volume datum at 0 time of exposure to the temperature chosen for initiating thermal degradation. The ratio conveniently displays the progressive increase in the retention of the basic probe as acidic surface properties develop in the polyolefines. The opposite paths followed in the two representations are clearly seen. The inherent agglomeration index C (Fig. 3) strongly correlates with E for both LDPE and LLDPE when these polymers are in their initial states of neutrality. The correlation coefficient drops rapidly below 0.9 after some 30 min of

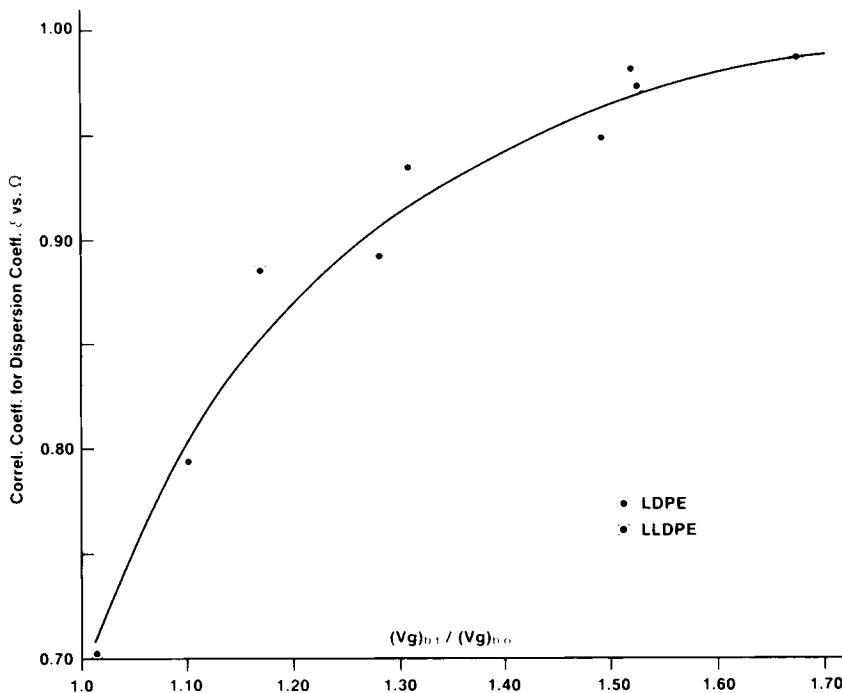


Fig. 4. Evolution of correlation coefficient for energy parameter E and pigment acid/base value Ω with changing acid/base balance in host polymer.

polymer residence time at 220°C, corresponding to a V_g ratio > 1.30 . The initial lack of correlation with Ω (Fig. 4) is evident at a coefficient value near 0.7. However, again as the V_g ratio rises above 1.30, the correlation coefficient increases above 0.9 to an apparent plateau in the range of 0.98.

The results presented here stress the great influence of surface coatings on the way in which particulate additives affect the performance of polymer systems. The various coatings applied to the present rutile pigments account for no more than 3–4% of the total solids weight, but they are dominant in determining the dispersibility of these solids. Fillers and pigments used in multicomponent polymer systems should therefore be selected on the basis of their surface structure, or their acid/base interaction potential, and not solely on their generic chemistry. The influence of surface coatings, and consequently that of interfacial phenomena, is by no means limited to dispersion processes.

In a recent communication,⁸ it was shown that the effectiveness of flow additives as suppressants of flow discontinuities in the melt processing of LLDPE varied with the choice of rutile pigments present as co-additives in the system. Specific interactions between the pigments and the flow additives appear to be responsible. Polymer melt rheology therefore also responds to the surface characteristics of particulates. This supports the suggestion that interaction phenomena, and particularly acid/base concepts, may have far-reaching consequences on the overall property balance displayed by given polymer systems.

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