Interfacial Interactions and Mechanical Properties of Filled Polymers

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Synopsis

Mechanical properties, notably the ductility of rutile-filled low-density polyethylene (LDPE) and chlorinated polyethylene (CPE), were studied to determine the influence of filler dispersion and of matrix-filler interactions. Potential interactions between polymer and filler were obtained from inverse gas chromatography, in the form of acid/base interaction parameters. The strength of filler aggregates was obtained from flow properties of the dry powders. Dispersion quality in molded specimens was identified from X-ray contact micrographs. The ductility of filled, nonpolar LDPE was found to be independent of acid/base considerations, but strong correlations have been drawn between the strength of filler aggregates and the quality of dispersion attained by controlled mixing methods. Inherent filler agglomeration thus also affects the mechanical properties of the nonpolar matrix. Coated, nonagglomerated fillers dispersed well, leading to ductilities at low filler load that exceeded that of the unfilled host polymer. In contrast, acid/base interactions were found to exert dominant influence on rutile dispertion in CPE. Similarly, the mechanical properties of this polymer varied with the acid/base forces acting at matrix/filler contacts.

INTRODUCTION

Research in our laboratories has been directed to an evaluation of interactions at contacts between polymers and additives generally found in composites, blends, and filled polymer systems.[1,2] The process of adding particulates to a polymer matrix is, of course, well known. It is practiced to improve such properties of the host polymer as stiffness, opacity, environmental stability, gas permeability, electrical conductivity, and so on. However, there are also adverse effects; toughness and ultimate elongation of filled polymers often suffer on adding fillers and pigments. Property modifications are functions, expectedly, of the quantity of filler added, but also of dispersion quality and of the adhesion at polymer/filler interfaces.[3,4] The widespread use of silanes and other agents as surface and interface modifiers undoubtedly relates to the adverse effects resulting from inadequate bonding when interactions between host and additive are unfavorable.

Despite the apparent importance of component interactions and of dispersion quality, discussions of these factors often are inadequate in communications on mechanical properties of polymers. The situation justifies the thrust of our work, the present paper being an extension of the earlier publications already noted.[1,2] In these it was shown that standard treatments applied to rutile pigments could result in pigment surfaces that were acidic, basic, or amphipatic.

Further, the cohesive strength of agglomerates also was found to vary significantly in a series of rutiles with different surface coatings. When added to a nonpolar polymer (low-density polyethylene, LDPE), inherent agglomeration was a major factor in dispersing the rutiles by a controlled mixing procedure, but the acid/base balance of the surfaces was of little consequence. A very different situation existed with polar polymer hosts, represented by chlorinated polyethylene (CPE)[2] and thermally modified LDPE and HDPE.[5] In these polymers, acid/base interactions at polymer/filler contacts were the major factors in determining particle dispersion and, consequently, the dynamic mechanical properties of the systems. The current paper is concerned with the role of acid/base interactions and of filler dispersion on the mechanical characteristics of filled polymers at high degrees of deformation.

EXPERIMENTAL

Materials

The LDPE, from Dow Chemical Canada, Inc., was a film-grade polymer with $M_w = 1.44 \cdot 10^5$ and $M_n = 3.04 \cdot 10^4$. It was compounded with 0.1% thermal stabilizer (Irganox 1010) prior to further use in formulating filled compounds. In selected cases, however, the polymer served as host after it had been sheared at 200°C for periods exceeding the induction time for thermal degradation, determined from scanning calorimetric data. As shown earlier,[5] the high-temperature shear exposure introduced polarity into the polymer.

The CPE was a Dow Chemical Canada, Inc., polymer, at 42% chlorination. The polymer was amorphous. It was dry blended with 2 phr calcium stearate and 0.5 phr stearic acid to guard against thermal degradation.

Nine rutile specimens were used. They were obtained courtesy of Tioxide Canada Inc. The pigments had very similar bulk characteristics, but were surface-modified by a variety of proprietary surface coatings. Their BET surface areas were found to lie in the range 7–9 m^2/g.

Acid/Base Properties

Acid/base interaction parameters for particulates and polymers were determined by inverse gas chromatographic (IGC) methods.[6] Procedures have been described in detail previously.[1,2] Following the theories of Drago and co-workers,[7] butanol and butylamine were selected as reference acid and base vapor probes. The retention volumes generated by these probes were then used to define the acid/base interaction number, Ω, according to

$$\Omega_a = 1 - (V_g)_b/(V_g)_a \tag{1}$$

and

$$\Omega_b = (V_g)_a/(V_g)_b - 1$$

where the V_g are the retention volumes and the subscripts denote acid and base materials.

Characterization indices for pigments and host polymers are reported in Table I. The positive values of Ω for pigments 3, 4, 5, and 6 show that these behave as Lewis bases. Rutiles 8 and 9 with negative Ω have surface coatings leading to acidic behavior, whereas 1, 2, and 7 may be considered as amphipatic. Clearly, the CPE is strongly acidic and, as expected of a surface lacking non-dispersive forces, the LDPE reports an Ω within experimental error of zero. The shear/temperature-modified version of LDPE, however, has a mildly acidic surface.

Inherent Agglomeration

The principles of powder rheology were applied to determine an inherent agglomeration index, C, for each of the rutiles. Details of the procedure have been reported in Ref. 2. Briefly, constant volumes of dry pigment were sheared in a Brabender mixer at constant mixing speed but under varying applied loads. Equilibrium torques generated by the sheared powder were recorded and plotted against the applied load. Excellent straight-line relationships resulted, in keeping with theory,[8] and the ordinate intercept was taken as the C parameter. It also is entered in Table I. Increasing C values indicate increasing agglomerate strength and rising resistance to dispersion. It is evident that surface coatings are capable of producing widely varying agglomeration tendencies in these pigments.

Compounding and Pigment Dispersion

Compounds with pigment volume fractions in the range 0.5%–20% were prepared with a Brabender mixer. Mixing temperature was controlled at 180°C, and a rotational speed of 50 rpm was used throughout. Blending was continued

TABLE I
Interaction and Inherent Agglomeration Indexes

Material	Ω Acid/base parameter	Inherent agglomeration parameter C (arb. units)
TiO$_2$-1	0.02	110
TiO$_2$-2	0.06	790
TiO$_2$-3	1.69	75
TiO$_2$-4	5.25	290
TiO$_2$-5	1.27	590
TiO$_2$-6	5.05	15
TiO$_2$-7	−0.02	300
TiO$_2$-8	−0.42	170
TiO$_2$-9	−0.50	0
LDPE	−0.03	—
CPE	−1.71	—
LDPE (sheared at 200°C)	−0.21	—

for 2 min beyond the attainment of steady-state torque readings. Basic rutiles 4 and 6, the former moderately agglomerated, the latter agglomerate-free (see Table I), were also used to form compounds with the LDPE host, using a Gelimat intensive-shear kneading blender. The intensively sheared compounds contained 3 vol % rutile and generated temperatures during the shearing operation that were sufficiently high to result in mild oxidation of the host polymer. The LDPE in these samples is therefore mildly acidic (see Table I). Milled compounds were compression molded at 180°C to produce plaques 0.05 cm thick. Plaques were quenched in cold running water and stored at room temperature for further use.

Dispersion quality was evaluated in LDPE compounds with 0.5% rutile, using X-ray contact micrography, as described earlier.[2] Statistical analysis[9] of contact micrographs led to calculations of a segregation index, I, which varies between the limits 1 and 0, dispersion quality increasing as I tends toward 0. These characterization data are reported in Table II. They suggest a relationship between the agglomeration index C and dispersion quality: For example, the highly segregated pigments 6 and 9 produce the lowest I values, whereas aggregated solids such as 2 and 5 disperse poorly, as shown by the high I values. Intermediate values of I apply to pigments at moderate aggregation, exemplified by rutiles 1 and 7.

Mechanical Properties

It is well known that the mechanical properties of polymers depend significantly on details of shear and thermal history. These variables were strictly controlled in all phases of sample compounding and preparation. Stress-strain data were obtained with an Instron tester on specimens cut in accordance with ASTM procedure D-638. Prior to testing, samples were conditioned at 23°C, 50% RH for 24 h. Samples were extended at a strain rate of 0.5 cm/min, and a minimum of four specimens of each formulation was involved. A reproducibility of ±5% applies to reported data for unfilled polymers and for compounds with up to 3 vol % filler. At higher loadings, the results have an uncertainty of ±15%. Accordingly, the bulk of work reported in this paper is restricted to specimens with filler loadings of 3 vol % or less.

TABLE II
Dispersion Quality Indexes for Rutile-Filled LDPE ($\phi_f = 0.005$)

Rutile #	$I \times 10^2$
TiO_2-1	3.2
TiO_2-2	10.0
TiO_2-3	2.1
TiO_2-4	18.0
TiO_2-5	11.0
TiO_2-6	1.0
TiO_2-7	5.2
TiO_2-8	2.6
TiO_2-9	1.1

RESULTS AND DISCUSSION

Polyethylene Compounds

Stress-strain relationships for compounds at two levels of rutile 1 and that for the control polyethylene are shown in Figure 1. The pattern is typical of other compounds: At higher pigment loadings, the ductility of compounds is significantly impaired and the tensile strength is reduced. Although it is not evident from Figure 1, the initial (Young) modulus is raised. All of these effects follow expected patterns.[10] Curiously, however, the curve for 0.5% rutile shows an ultimate elongation somewhat greater than that for the unfilled polymer. The tensile strength also has been increased by the presence of the rutile at this low concentration. Detailed examination of mechanical responses confirmed that initial moduli and yield points responded uniformly to the quantity of rutile present, but did not distinguish among the various surface treatments applied to the pigments. Attention is focused therefore on the elongation at break and the tensile strength of compounds, where the effect of surface conditioning becomes important.
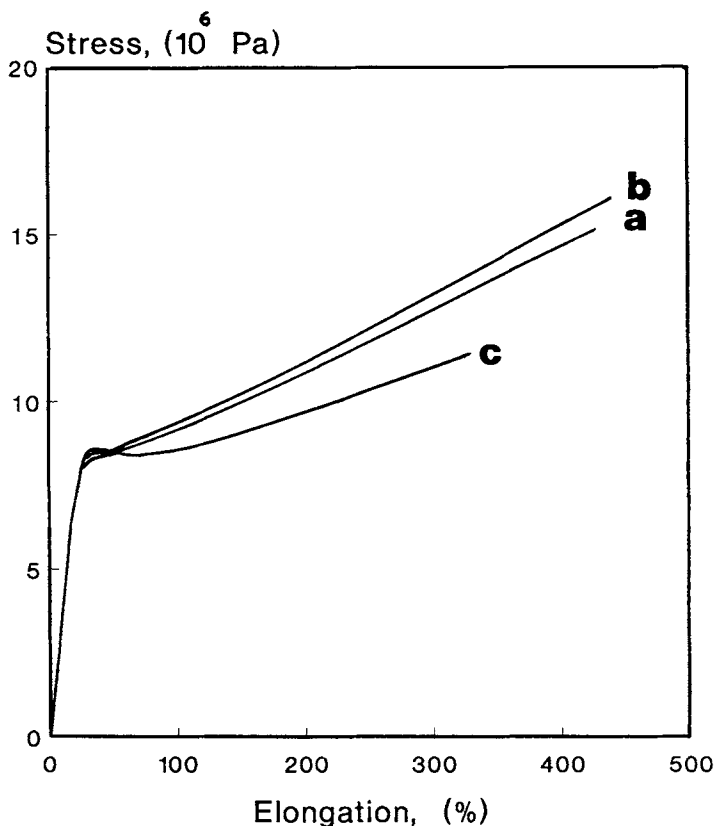

Fig. 1.   Stress-strain curves for LDPE with TiO_2-1 filler. Vol % filler: (a) = 0; (b) = 0.5; (c) = 3.0.

A summary of pertinent results is given in Table III. Particularly at low pigment concentrations, ultimate properties are clearly affected by the condition of the polymer-filler interface. Elongation-at-break may be considered in terms of Nielsen's model,[10] which states that

$$\epsilon_{bf} = \epsilon_{bp}(1 - \phi^{1/3})$$ (2)

where ϵ_{bf} and ϵ_{bp}, respectively, are the elongations of filled and pure polymer and ϕ is the volume fraction of particulates. The model assumes that spherical particles are uniformly dispersed and that there is strong adhesion at the polymer/filler interface. The strong decrease in ductility at low filler concentrations is affected by the adhesion factor. When adhesion is poor, a separation at particle/matrix contacts occurs due to the formation of voids or microcavities when the specimen is subjected to elongational deformations[10,11]; as a result, well-dispersed but weakly adhering particulates produce compounds with higher ultimate elongations.

The predictions of eq. (2) are compared with the performance of present compounds in Figure 2. For simplicity, only three of the rutiles are represented. Very broad variations in the ratio $\epsilon_{bf}/\epsilon_{bp}$ occur at low levels of rutile loading. Compounds with rutile 1 are slightly more extensible than are unfilled control polymers. The pigment is the only one in the present set that is amphipatic and nonagglomerated. In a nonpolar matrix like LDPE, pigments of this type will be readily dispersed by mixing techniques such as the Brabender method used here. The low I value (Table II) for this case confirms the statement. The basic, but nonagglomerated, rutile 6 produces compounds at 0.5% loading in which the ductility is essentially equal to that of the unfilled polymer. We suggest that due to the uniform, fine dispersion of particles, some 0.5 μm in diameter in these cases, the morphology of the host may be shifted toward a reduced degree of crystallinity. This would account for the rise in ductility. Another possibility is the existence of local, intensive shear fields in the im-

TABLE III
Ultimate Properties of Filled Polyethylene Compositions

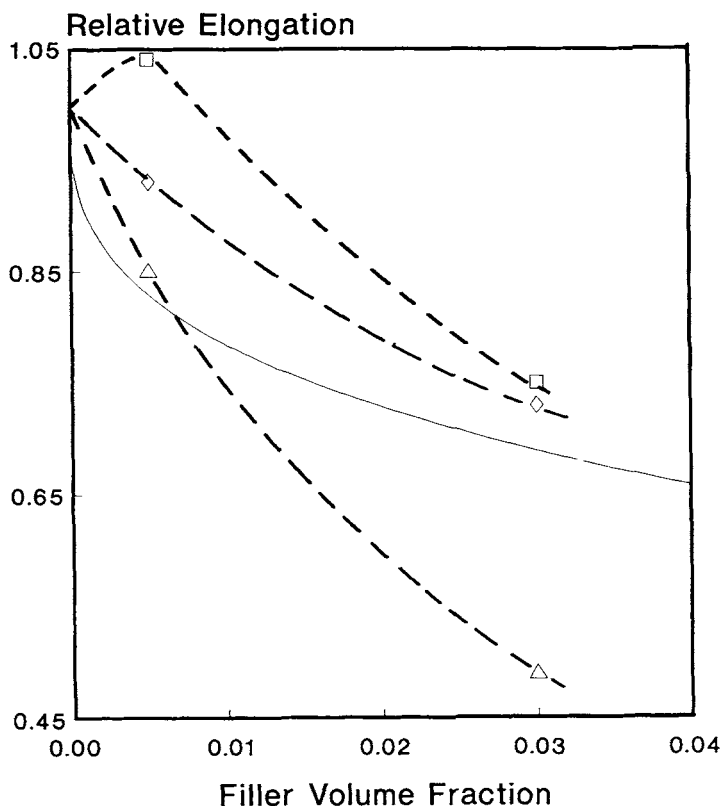| Rutile sample	ϕ (%)	$\sigma_B \times 10^{-6}$ (N m^{-2})			ϵ_B (%)		
		0	0.5	3.0	0	0.5	3.0
TiO$_2$-1		15.9	16.1	11.4	427	444	321
TiO$_2$-2			13.6	12.3		405	253
TiO$_2$-3			15.5	16.6		423	382
TiO$_2$-4			14.8	8.6		362	208
TiO$_2$-5			15.7	14.0		399	310
TiO$_2$-6			16.7	12.5		434	355
TiO$_2$-7			17.2	11.4		424	263
TiO$_2$-8				12.5			292
TiO$_2$-9				14.5			400
TiO$_2$-4	(intensive shear)			12.6			349
TiO$_2$-6	(intensive shear)			14.4			389

Relative Elongation

Fig. 2. Relative elongation at break vs. filler volume fraction of LDPE systems: (□) TiO$_2$-1; (◇) TiO$_2$-5; (△) TiO$_2$-4; (———) eq. (2).

mediate vicinity of well-dispersed, agglomerate-free particles. Many properties of LDPE are known to respond to intensive shear,[12] partial disentanglement being one of the proposed mechanisms.[13]

Further comparison of results in Tables I–III shows no apparent correlation between the ϵ_{bf} parameter and the acid-base number Ω. Surface acidity or basicity in the filler surface is of little consequence in determining the state of adhesion at contacts with the nonpolar LDPE. On the other hand, as already inferred, a correlation does exist between the ultimate ductility and the degree of dispersion attained in the compound. This is demonstrated in Figure 3, where the relative ductility quotient is plotted against the I parameter. The advantage, in terms of retained ductility in filled compounds, of using pigments with low degrees of inherent agglomeration is evident. In practice, of course, the effects of inherent pigment agglomeration, shown here, could be controlled by the use of more intense shear fields, thus attaining adequate dispersion quality. The data, in Table III, for intensively mixed versions of compounds with the agglomerated rutile 4 are relevant to this point. At 3% loading, the intensively sheared compound gives a tensile strength 50% greater than that of the weakly sheared Brabender compound and an ultimate elongation that
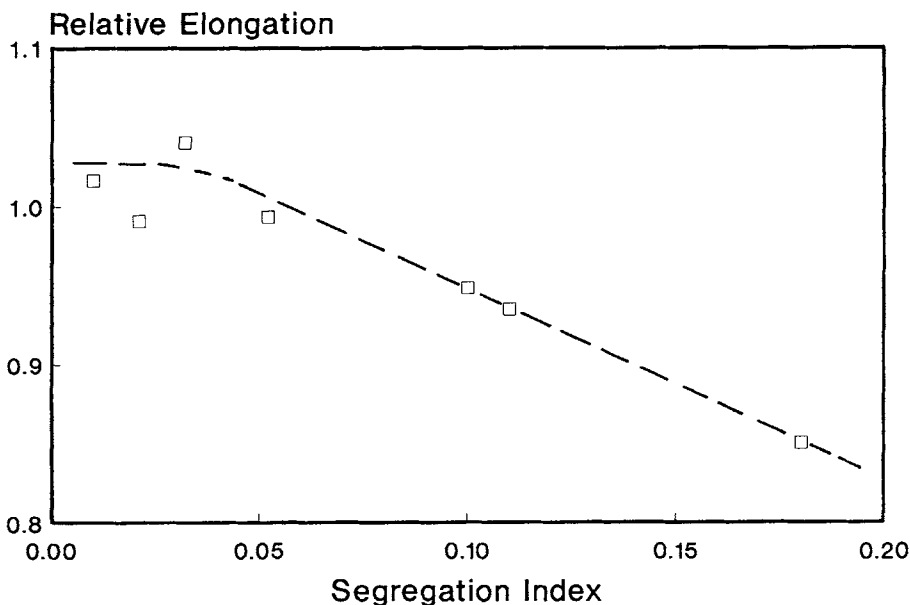
Relative Elongation

Fig. 3. Variation of relative elongation at break with pigment dispersion: LDPE host, pigment vol fraction = 0.005.

improves dramatically, by about 75%. A contributing cause to performance improvement in this case is the mild acidification of the LDPE host. The results for intensively sheared versions of rutile 6 compounds point to this factor. The rutile has a very low C number and, therefore, disperses very well even under the mild, control dispersion conditions. Like rutile 4, it is coated to give strong surface basicity. The intensively sheared analog gives a rise of about 15% in tensile strength and of roughly 10% in ductility. In keeping with our earlier conclusions,[1,2] acid/base interaction begins to exert appreciable influence on mechanical properties as soon as it is able to function.

The marked decrease in ductility with decreasing dispersion quality, documented in Figure 3, may be viewed in terms of known rupture mechanisms in polymers, for example, as given by Nielsen.[10] In an unfilled polymer, rupture initiates at a weakness in the structure when local stress builds up at this point as a result of the deformation process. The local rupture event then propagates through the bulk specimen. In a filled polymer, failure may initiate in the matrix, as before, or at polymer/filler interfaces, or within agglomerates of the particles. It is reasonable that in a poorly dispersed, agglomerated pigmented compound the weakest link in the solid is within the agglomerate itself. A weak point within the agglomerate will fail through particle slip at relatively low applied stresses, then act as a stress concentrator and will propagate rupture through the bulk specimen again at relatively low applied stress. Compounds with agglomerated rutiles, such as #2 and #4, fail at low ductility and strength, in contrast with the superior behavior of compounds with rutiles 1 and 6, consistent with this suggestion.

Filled CPE Compounds

The stress-strain curves for control and filled versions of CPE are illustrated by typical examples in Figure 4. Unlike LDPE, CPE is an elastomeric polymer, exhibiting a sigmoidal stress-strain curve at room temperature, with an extension-at-break of 850%. Specimens recovered their original shape following rupture, showing that the combination of hydrogen bonds and chain entanglements was effective in establishing strong recoverable elastic properties even in the absence of chemical crosslinks. Appreciable elastic recovery was observed even in highly filled specimens, e.g., containing up to 20 vol % pigment.

As in the case of LDPE compounds, particular attention is given to the ultimate property parameters, with a summary of results in Table IV, at the moderate filler level of 3 vol %. Whereas in LDPE compounds tensile strengths varied broadly with rutile type (see Table III), only relatively small variations are observed here. Again, unlike the former case, the tensile strength always rises in the presence of the pigment. Given the existence of finite adhesion at all polymer/filler interfaces of this system, the increase in σ_b may be due to the fact that at any elongation of the specimen the actual extension of a mac-
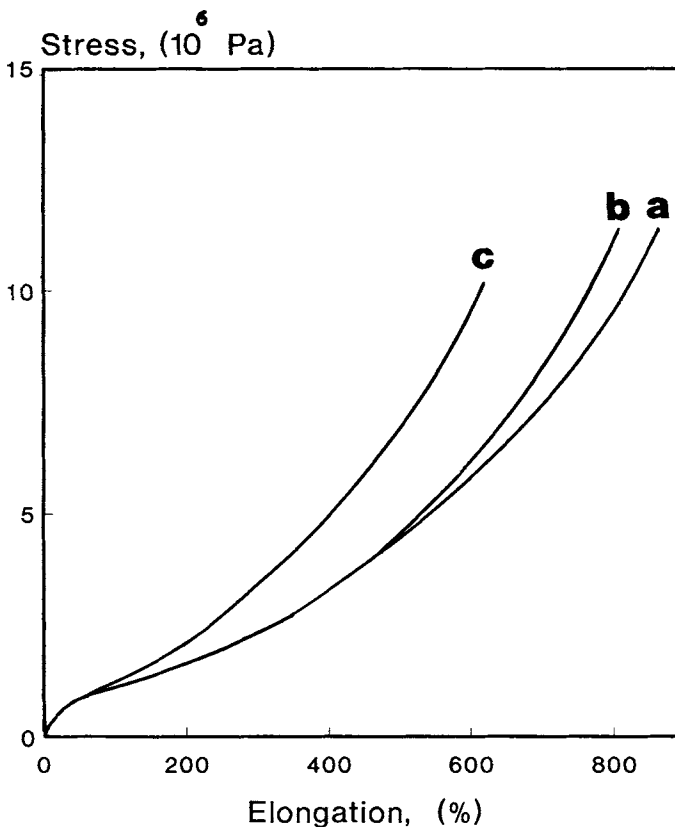

Fig. 4. Stress-strain curves for CPE with TiO_2-3 filler. Vol % filler: (a) = 0; (b) = 3.0; (c) = 20.

TABLE IV
Tensile Properties of Filled CPE Compositions

Sample CPE + 3%	$\sigma_b \times 10^{-7}$ (N m^{-2})	ϵ_b (%)
	1.16	846
TiO$_2$-1	1.27	932
TiO$_2$-2	1.17	844
TiO$_2$-3	1.18	791
TiO$_2$-4	1.19	685
TiO$_2$-5	1.29	802
TiO$_2$-6	1.22	765
TiO$_2$-7	1.36	799
TiO$_2$-8	1.24	840
TiO$_2$-9	1.40	851

romolecule in a filled specimen is greater than in an unfilled counterpart. Ductilities also vary less dramatically here, although the maximum variation (between compounds with rutile 1 and those with #4) of some 25%–30% is certainly significant.

We have stated previously[2] that, in the CPE matrix, generally finer dispersions of rutile were obtained than was the case with LDPE. Consequently, it seems unlikely that the mechanical property effects depend on the inherent degree of agglomeration in the pigments. Indeed, an inspection of results in Tables I, II, and IV does not point to any obvious relationship between the C index of rutiles and ϵ_b. More likely, therefore, is a link with the acid/base interaction factor at polymer-filler contacts. The presence of such interactions will result in the formation of an adsorbed, immobilized polymer layer, the dimensions of which may be inferred from dynamic mechanical measurements.[1,2] The thickness of the immobilized layer should increase with the strength of acid/base interactions, that is, in terms of the present approach, with the difference $\Omega_f - \Omega_p$. For large values of this difference, strongly bonded and relatively thick layers of polymer should be associated with the dispersed, agglomerate-free particles. The locus of failure in extension for such cases should be in the immobilized layer, which will act as a powerful stress-concentration center. Failure may be expected to occur at relatively low extensions. As the difference in Ω values approaches zero, acid/acid or base/base rejection should lead to microvoid formation in the region of the interface. The situation should resemble more closely the case of unfilled polymer, that is, with failure occurring at higher elongations and as a result of events such as chain rupture or entanglement slip. A consequence of these arguments is a relationship between relative elongation and the difference $\Omega_f - \Omega_p$, of the type seen in Figure 5. The experimental data therefore are consistent with the hypotheses put forth here and in our preceding papers.

CONCLUSIONS

The results of this research show that

- Surface coatings applied to commodity pigments such as rutile, affect the acid/base interaction potential of the surfaces and the degree of inherent agglomeration in the colorant.
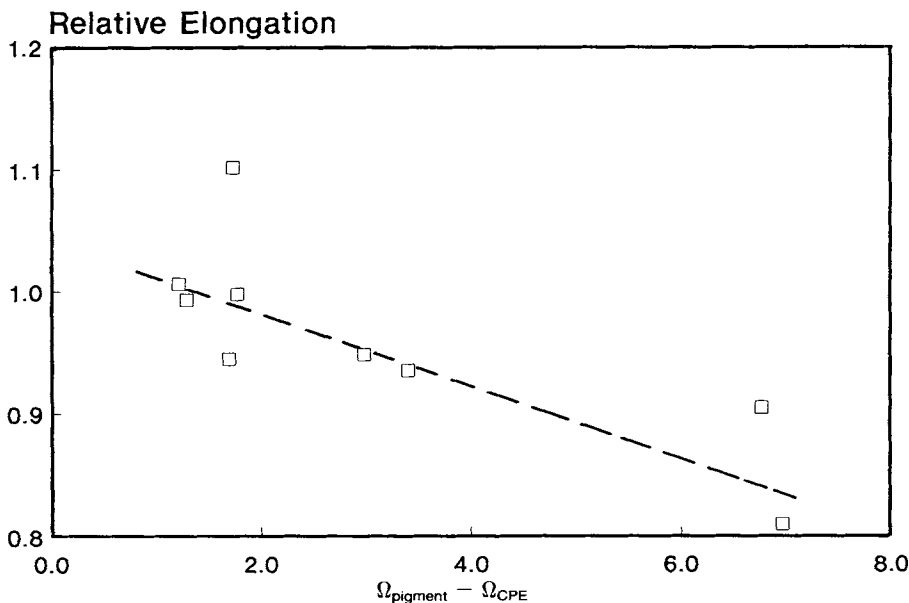
Relative Elongation

Fig. 5. Relative elongation at break and interaction at pigment-polymer contacts in CPE host: Rutile vol fraction = 0.03.

- In the absence of strong polar interactions at polymer-filler contacts, tensile strength and elongation at rupture of pigmented polymer samples depend on the quality of particle dispersion. This was demonstrated for a low-density polyethylene host. Property improvements are realized by ensuring uniform dispersion.

- In polar polymers, exemplified by CPE and thermally modified LDPE, mechanical properties at large deformation depend on the degree of acid/base interaction, as determined from parameters measured by IGC. Elongation at break is improved at lower strengths of acid/base interaction. However, tensile strength, and mechanical parameters at lower extension, benefit from acid/base coupling.

- Different mechanisms for failure appear to be operative in filled compounds with and without acid/base interaction. In the former, failure seems to initiate in a polymer layer immobilized in the particle interface by acid/base forces. In the latter, failure appears to be associated with more classical causes, such as the rupture of polymer chains or the slip of chain entanglements.

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