Surface Interactions and Some Properties of Filled Polymers

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Synopsis

Inverse chromatography was applied to evaluate interaction parameters for polyethylene (PE), polyvinyl chloride (PVC), and $CaCO_3$, these parameters being based on retention volumes of proton-donor, -acceptor, and neutral vapors. The acid/base characteristics of $CaCO_3$ were controllably altered by exposing the particulate to microwave plasmas sustained by acidic and basic vapors. It was shown that the ease-of-dispersion of fillers in the polymer matrixes related with the acid–base interaction balance in the polymer-filler pair, and varied widely with the surface treatment given to the filler. Mechanical properties at large deformation of the filled polymers and their durability also were shown to depend on surface interactions. Optimization of properties in PVC compounds was favored when strong acid-base interactions could take place with the plasma-modified filler. In the case of PE, properties were superior when unmodified filler was used; imparting strongly acidic or basic surface properties to the filler diminished its "compatibility" and usefulness with this nonpolar matrix.

INTRODUCTION

Reducing the energy requirements for processing multicomponent polymer systems and, similarly, optimizing their mechanical properties and their persistence represent objectives of obvious importance for the future of energy-intensive polymeric materials. This study relates to the above objectives and approaches the problem through the selective modification and control of interfacial properties in multicomponent systems. The fundamental component of this study lies in furthering an understanding of the relation involving component "compatibility" (i.e., miscibility), the interfacial properties, and selected bulk properties of multicomponent polymer systems, a subject of widely recognized interest.[1] The availability of two experimental approaches has spurred the present work: First is the capability of inverse gas chromatography (IGC) to provide useful information on component interactions in polymer systems.[2] While reservations on the breadth of application for IGC data must be recognized,[3] the method, nevertheless, presents a convenient and flexible approach to the estimation of thermodynamic interactions in macromolecular compositions. Second is the capability of modifying the surface properties of solids by treatment in plasma discharges. In our laboratories, a large volume microwave plasma (LMP) installation[4] has been used to modify the surface properties of a wide variety of solids. In particular, we refer to recent studies in which plasma-modified fillers were used as coupling agents in incompatible polymer blends.[5,6]

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In the present work we report on the dispersion behavior of $CaCO_3$ fillers in polyethylene (PE) and polyvinyl chloride (PVC). Selected mechanical properties of the filled compounds were evaluated along with their change on aging at elevated temperatures. An effort has been made to rationalize observations in terms of interactions at polymer/filler contacts. In so doing we have followed the precedent of Fowkes and co-workers,[7,8] who used acid–base interaction criteria to account for the magnitude of surface and interfacial parameters in polymers. These criteria of interaction follow from the proton donor/acceptor theories of Drago et al.[9] In principle, acid–base characterization parameters can be assigned to polymers, fillers, etc., and the compatibility of materials then judged on the basis of the strength of their acid–base interactions. The evaluation of acid–base parameters for simple organic and inorganic materials is relatively straightforward, calorimetrically measured heats of solution or mixing in standard media being a suitable experimental route. In the case of polymers such as PE and PVC, however, calorimetry would be both tedious and restricted to a narrow temperature range. On the other hand, as already suggested in a previously published article,[10] IGC data appear to be well suited for the evaluation of the desired parameters, and this was the experimental route again followed here. In order to define the acid/base characteristics of PE, PVC, and of $CaCO_3$ fillers, we determined the retention volumes of vapor probes selected from Drago's tabulation,[9] these vapors representing proton-donor, proton-acceptor as well as "neutral," nonpolar species. In this respect, a similarity is noted with the interpretation of IGC-based compatibility studies reported by Olabisi.[11] Since IGC data are readily measurable over an appreciable temperature range, it was possible to specify the desired interaction criteria for polymer/filler pairs from use temperatures to temperatures near the processing range.

Similar to the above considerations, Drago's acid/base parameters were used to select vapors for LMP modifications of filler surfaces. Amine and alcohol vapors were thus employed in attempts to produce, respectively, basic and acidic shifts in the properties of the $CaCO_3$ and so to modify, controllably, the strength of acid–base interactions at filler/polymer contacts.

EXPERIMENTAL

Materials

The PE sample used in this work was a Phillips Petroleum Co. linear polymer with $M_v = 1.60 \times 10^5$, as determined from the intrinsic viscosity in Tetralin at 140°C. The polymer was compounded with 0.1 wt % antioxidant (Santonox) prior to its further use in the formulation of filled compositions.

The PVC sample, a K67 resin supplied by Exxon Canada Ltd. and already used in earlier work,[10] was dry blended with 3 phr dibasic lead stabilizer and 20 phr di-iso-octylphthalate plasticizer prior to further use. In all subsequent references to PVC matrix polymer, it is this composition which is involved.

A commercial sample of precipitated $CaCO_3$ without prior surface treatment was used as filler. The surface area, determined from BET isotherms, was 5.5 m^2/g, and microscopic analysis showed the mean particle size to be 1.2 μm.

IGC Measurements

A Perkin-Elmer dual-column gas chromatograph with thermal conductivity detector was used for retention time measurements in the range 25–90°C. Oven temperature was controlled to ±0.5°C. Detailed procedures for the preparation of PVC and PE columns have been described previously.[12,13] The polymers were coated onto 60–80 mesh, AW-DMCS-treated Chromosorb W, to give an 8.3% loading of PVC and a 7.9% loading of PE. Xylene was the solvent for PE, THF for PVC. The $CaCO_3$ was mixed intimately with H012 (200–300 μm) glass beads in a weight ratio of 1:5 favoring the glass, and the dry blend loaded into columns to contain between 0.50 and 0.85 g of $CaCO_3$. A dummy column of glass beads was used for calibrations permitting calculation of the true interaction quantities for $CaCO_3$–probe pairs. Three probes were involved in these experiments. The basic probe was n-butylamine, the acid prototype was t-butyl alcohol, and n-octane was the neutral volatile phase. Retention volumes V_g^0 were measured in at least quadruplicate, and in some cases in more numerous repetitions. For polymer stationary phases the repeatability in V_g^0 was ±2%, but a somewhat higher variability (±4%) occurred with $CaCO_3$/glass substrates. The retention of vapors by glass beads was of minor importance at lower temperatures, but, at 90°C, a correction of about 3% in V_g^0 was indicated and applied.

Surface Modifications

Microwave plasma treatment of $CaCO_3$ was performed on apparatus which has been described previously.[4–6] The tubular LMP quartz reactor was loaded with about 30 g filler and the surface activated in Ar plasmas for 60 s prior to acid or basic modification. To achieve such modifications, t-butanol and n-butyl amine again were the selected vapors. In plasma treatments, substrate temperatures were near ambient, monomer pressures were 0.5–2.0 Torr, and plasmas were sustained at 200 W total power for 180 s, in pulses of 20-s duration.

Microwave plasmas, operating at 2.45 GHz, fragment the plasma-producing vapor and form crosslinked polymeric species on the substrate. Though generically similar to the monomer, plasma polymers have distinctive structures.[14] Those produced by the monomers used in this case have not been characterized as to structure. Filler samples were conditioned in Ar for 5 min following plasma treatment to allow surface reactivity to decay, and were then stored in desiccators for further use.

Blending, Mechanicals, and Aging

A Brabender Plasticorder was used to produce filled PE and PVC samples containing 20 and 40 wt % $CaCO_3$. As in an earlier study,[10] PVC was compounded at 170°C, while PE blends were prepared at 190°C wall temperature. In all cases the Brabender was operated at 50 rpm, and the total volume of material in the mixing chamber was maintained constant. Mixing was continued until an equilibrium torque value was attained, this being marked by constant torque for at least 2 min of operation. Mixing behavior was expressed by two parameters; the first of these was the energy requirement to attain constant torque, ϵ_r. This was obtained by integrating under the torque–time curve. The second parameter, critical mixing time (cmt) was the time needed to attain steady-state

torques. These parameters are considered to be indexes of the ease-of-dispersion. They do not, however, inform on the fineness (quality) of dispersion, except indirectly as judged from mechanical properties and their durability.

Mechanical properties at failure for filled PVC and PE stocks were measured at room temperature using an Instron table-model tensile tester and jaw separation rates of 0.5 cm·min^{-1}. All reported data are averages of five determinations. To normalize tensile responses for variations arising from thermal history effects,[15] specimens for tensile testing were compression molded at 190°C and cooled to room temperature by quenching in running, cold water. Cut test specimens were then conditioned for 24 h in the controlled temperature and humidity chamber of the Instron Tester, prior to performing the test. An estimate of the durability of mechanical properties was made by storing PVC stocks at 100°C and PE stocks at 70°C for up to 2 weeks, and periodically retesting as noted above. In this sequence also, specimens were conditioned for 24 hr in the environment of the tensile tester prior to being used. Unfilled, control samples of PVC and PE were aged similarly and then examined by scanning calorimetry. The thermal traces for aged and control specimens were essentially identical, indicating that no significant chemical changes occurred during the aging process.

RESULTS AND DISCUSSION

Interaction Characteristics

IGC evaluations of V_g^0 at 30°C, 60°C, and 90°C were the basis for characterizing the inherent acidlike or baselike properties of PVC, PE, and filler surfaces. The data are summarized in Table I. Three sets of values are entered for $CaCO_3$ at each temperature. The first of these is for $CaCO_3$ as obtained. $CaCO_3$-a and $CaCO_3$-b data refer to plasma-modified surfaces, the former having been treated in a t-butanol plasma, the latter in a plasma sustained by t-butyl amine vapor.

Analysis of the results in Table I shows important differences in the retention characteristics, by the various solids, of the selected vapors. The strong retention

TABLE I
Summary of IGC Data: Inference of Acid/Base Interaction Values

	Stationary phase				
	PE	PVC	$CaCO_3$	$CaCO_3$-a	$CaCO_3$-b
V_g^0 (ml·g^{-1}) at 30°C for					
n-Octane	33.7	11.6	2.4_4	2.8_8	2.5_7
n-Bu. amine	18.4	19.3	4.2_0	6.3_4	2.9_5
t-Bu. alc.	20.9	8.6_7	5.3_6	3.7_2	8.1_8
60°C					
n-Octane	24.4	7.0_7	1.3_3	2.0_0	1.5_1
n-Bu. amine	11.7	14.8	2.6_7	5.1_5	2.0_6
t-Bu. alc.	13.5	5.2_9	3.3_8	2.4_3	6.2_7
90°C					
n-Octane	13.6	4.6_0	0.7_7	1.1_6	1.0_4
n-Bu. amine	6.9_2	9.9_3	1.9_2	3.1_0	1.4_3
t-Bu. alc.	7.74	4.1_1	2.3_8	1.8_6	3.8_8

of n-octane by PE contrasts with its lower, roughly equal retention properties for the acidic and basic probes. The PE thus, expectedly, appears to have neither donor nor acceptor tendencies; the relatively high V_g^0 values for this polymer are accounted for by the fact that the determinations were carried out well above the T_g for PE. Again as expected,[7,8,16] PVC has distinctively acid characteristics, the interaction with (retention of) n-butyl amine exceeding that of the other probes by a considerable margin. The response of $CaCO_3$ is particularly interesting, the filler as received behaving in an amphiphatic manner. On the other hand, strong shifts in donor-, acceptor-tendencies are created by LMP treatments. The strong retention of the basic probe by $CaCO_3$-a, and that of t-butanol by $CaCO_3$-b, attest to the apparent effectiveness of plasma surface conditioning.

The effect of temperature on V_g^0, as shown in Table I, while significant, does not produce important changes in the relative interaction tendencies of the substrates involved in this study. For practical reasons the IGC work was limited to 90°C, thus falling somewhat below the processing temperature range. In view of the systematic T dependence of V_g^0, however, it is reasonable to assume that the interaction patterns given in Table I will persist at processing as well as at use temperatures of the filled polymer systems.

While V_g^0 data in Table I seem useful in specifying the interaction tendencies displayed by a given solid surface, the absolute V_g^0 values may be inconvenient for use as parameters in correlations with other properties of the polymer–filler combinations. This is because V_g^0 may be influenced by such variables as the relative values of T_g and experimental temperature, by details of column preparation and the total volumes of probe species injected.[17] A normalized acid/base interaction parameter Ω was therefore defined by

$$\Omega = (V_g^0)\text{acid}/(V_g^0)\text{base}$$

where, in the present case, the retention volumes refer to t-butanol and butyl amine probes, respectively. The definition of the dimensionless parameter is arbitrary and based solely on considerations of experimental convenience. Table II lists Ω values for the materials of this study. Ideally a neutral substrate should have $\Omega = 1$, while for increasingly acidic or basic surfaces Ω should shift toward zero and to high positive values, respectively. The Ω parameter thus differentiates strongly among the solids of this work, clearly shows the effects of plasma-induced surface modifications in $CaCO_3$ and again indicates the relative constancy of the acid–base interaction balance in the 30–90°C range.

TABLE II
Acid/Base Interaction Parameter Ω[a]

	30°C	60°C	90°C
PE	1.14	1.15	1.12
PVC	0.45	0.36	0.41
$CaCO_3$	1.28	1.27	1.24
$CaCO_3$-a	0.59	0.47	0.60
$CaCO_3$-b	2.77	3.04	2.71

[a] Ratio of V_g^0 for t-butanol and n-butyl amine; see text.

Dispersion Behavior

The parameters describing the dispersion behavior of $CaCO_3$ fillers in PE and PVC matrixes are entered in Table III. For simplicity, only the relative proportions of the host polymer and filler are given, though, as stated earlier, plasticizers and stabilizers are included in each formulation. The mixing energy requirement parameter, ϵ_r, is expressed in arbitrary (area) units. The reproducibility of ϵ_r is less satisfactory than that of cmt, due partly to erratic initial peaks in the torque vs. time trace of the Brabender operation. We presume that pigment clusters of nonuniform size may be involved and that their shear-induced breakup in early stages of mixing accounts for this observation. The cmt parameter is considered to be a more reliable descriptor of the mixing process, at least for the present discussion.

The results in Table III show that both ϵ_r and cmt vary significantly with the type of $CaCO_3$ used, and therefore are sensitive to interactions at contact surfaces between filler and molten polymer. Qualitatively, surface treatments to $CaCO_3$ introduced by LMP processes do not enhance its dispersion behavior in PE. This is noted in the cmt value, which is increased for both $CaCO_3$-a and $CaCO_3$-b, relative to the unmodified solid. In term of the acid/base interaction concept, the neutral polymer appears to interact most favorably with the "neutral" or "amphipatic" surface of the untreated filler. In contrast, the strongly acid PVC fluid emphatically favors contact with $CaCO_3$-b, the cmt value being some 20% lower than for the untreated $CaCO_3$, and less than half of the corresponding time requirement for dispersing filler which had been modified to produce acidic surface properties.

The relationship between dispersion time requirement and acid/base interactions is shown more explicitly in Figures 1(A) and (B). Here the difference $\Omega_p - \Omega_f$ (the subscripts refer to polymer and filler, respectively) is used as an index of the interaction strength. The minimum in Figure 1(A) defined by PE/$CaCO_3$ pairs is evident; similarly, the low value of cmt for $CaCO_3$-b in PVC [Fig. 1(B)] contrasts sharply with the high cmt value obtained at $\Delta\Omega = (\Omega_p - \Omega_f) \simeq 0$. If a link between cmt and dispersion rate is assumed to exist, we may conclude that in melts such as PE, where only dispersion forces are involved in bonding with the filler, most rapid dispersion occurs when $\Delta\Omega \rightarrow 0$. On the other

TABLE III
Filler Mixing Parameters in PE and PVC

	Compound													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Wt %														
PE[a]	100	80	80	80	60	60	60	—	—	—	—	—	—	—
PVC[b]	—	—	—	—	—	—	—	100	80	80	80	60	60	60
$CaCO_3$	—	20	—	—	40	—	—	—	20	—	—	40	—	—
$CaCO_3$-a	—	—	20	—	—	40	—	—	—	20	—	—	40	—
$CaCO_3$-b	—	—	—	20	—	—	40	—	—	—	20	—	—	40
ϵ_r (arb. units)[b]	12.7	14.5	13.5	12.5	17.0	15.5	16.0	15.5	18.0	11.5	19.0	19.5	11.0	21.5
Variance ±	2.0	2.0	1.5	2.0	2.5	2.5	2.0	2.0	2.5	2.5	2.0	2.5	3.0	2.5
cmt (s)[b]	220	300	370	350	380	430	430	310	400	≥600	325	460	≥600	370
Variance ±	20	15	20	15	25	30	25	25	30	—	20	15	—	30

[a] For detailed composition of PE and PVC matrix, see text.

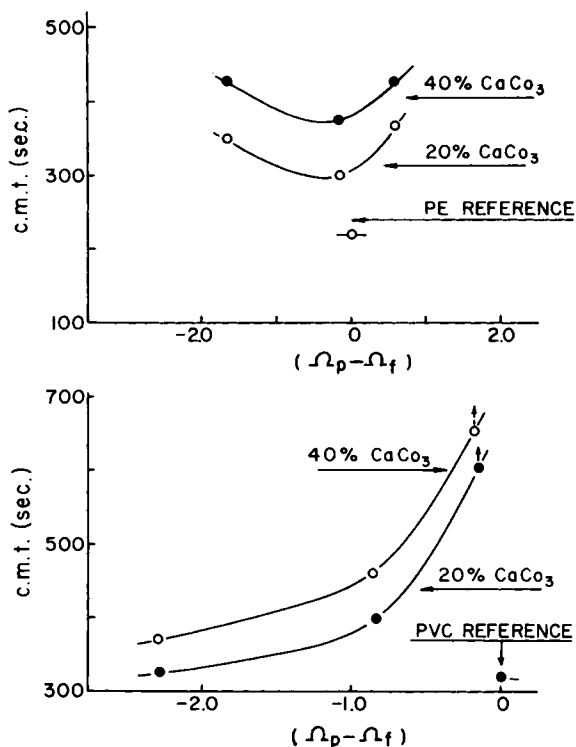[b] Mixing parameters as defined in text.

Fig. 1. Apparent link between acid/base interactions and mixing effectiveness: (A) $CaCO_3$/PE; (B) $CaCO_3$/PVC. Reference point indicates cmt for unfilled polymers.

hand, when associative forces are involved, dispersion rate varies with increasing absolute values of $\Delta\Omega$. Speculatively, in Figure 1(B), a maximum should be observed at $\Delta\Omega = 0$; in other words, fillers which are significantly more acidic than PVC itself, again, would have lower cmt values. Further work will be conducted to elaborate on this, and to show whether or not these guidelines to dispersion behavior apply to polymer/filler systems generally.

Judging from the results in Table III, ϵ_r varies roughly inversely with cmt. At first this seems surprising, but the observation may be related to the degree to which fillers disperse in the polymer matrixes. At present we cannot comment on the *quality* of dispersion attained in these experiments. The inverse relationship alluded to could be accounted for if that quality were also determined by the $\Delta\Omega$ factor. Then, strongly interacting systems would generate a relatively high ϵ_r value, suggesting fine dispersion. In weakly interacting systems, however, ϵ_r would remain low if filler clusters were not dispersed or only partially dispersed by the mixing process. Again more detailed studies are planned to clarify the issue.

Mechanical Properties, Time-Dependent Changes

The mechanical properties of filled polymers have been studied intensively.[18] It is recognized that adhesion or wetting at the polymer/filler interface can produce important effects, though correlative equations (Kerner or Halpin–Tsai)

do not account for possible perturbations from this source, assuming instead the existence of strong adhesion between filler and matrix phases. In the systems under study here, deformations in the linear range of behavior do not in fact appear to be influenced by surface interactions. This was already evident in earlier work[10] and is shown clearly in Figure 2, which compares the stress–strain curves for PVC containing 20 wt % of the $CaCO_3$ fillers used in this work. The elastic moduli for the three compounds are indistinguishable in this comparison, and the effects of surface conditioning become evident only in and beyond the yield–stress region. Empirically the effect is attributable to the distinct interaction balances at the filler/polymer interface; as noted already, it is possible that distinct degrees of dispersion were also attained under our normalized mixing conditions, so that the *effective* filler volume fractions in the three cases may also differ. In that case, the curves in Figure 2 could be interpreted in terms of yielding/dewetting concepts, for example as suggested by Nicolais and Narkis.[19]

The strong dependence of mechanical responses at large deformation to the condition of the polymer–filler interface is demonstrated by the ultimate tensile strength (UTS) in Figure 3 and elongation at break (E_b), in Figure 4. The data follow patterns similar to those shown by the mixing parameters discussed earlier. In the PVC system, where associative forces can exist at polymer–filler contacts, LMP treatments of $CaCO_3$ produce highly visible effects. The shift to basic surface properties in $CaCO_3$-b produces enhancement in ultimate properties which persist to the 40% loading level. The effect is more pronounced in E_b (Fig. 4), but significant also in the UTS value. An acidic shift in surface properties ($CaCO_3$-a) leads to performance which is much inferior to that in compounds with $CaCO_3$-b and also to materials with unmodified filler. A one-to-one correlation between property enhancement at failure and $\Delta\Omega$ is here strongly suggested.

In the PE matrix, where only dispersion force interactions are involved, the response to filler surface modifications is very mild. In all cases the more polar, LMP-modified fillers are less effective than the unmodified $CaCO_3$.
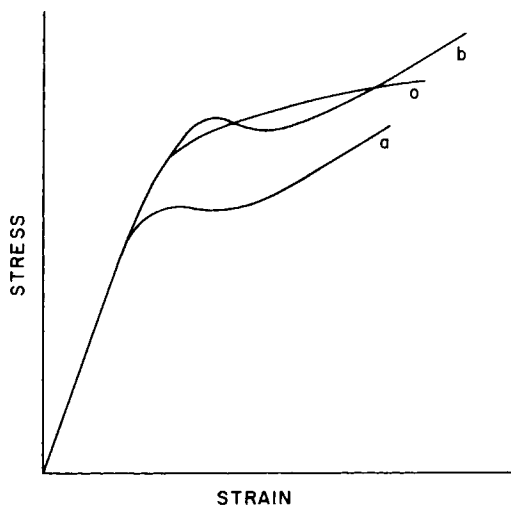

Fig. 2. Stress/strain curves for PVC/20% $CaCO_3$: Effect of surface conditioning by LMP: (O) Unmodified filler; (a) acid-modified filler; (b) base-modified filler.
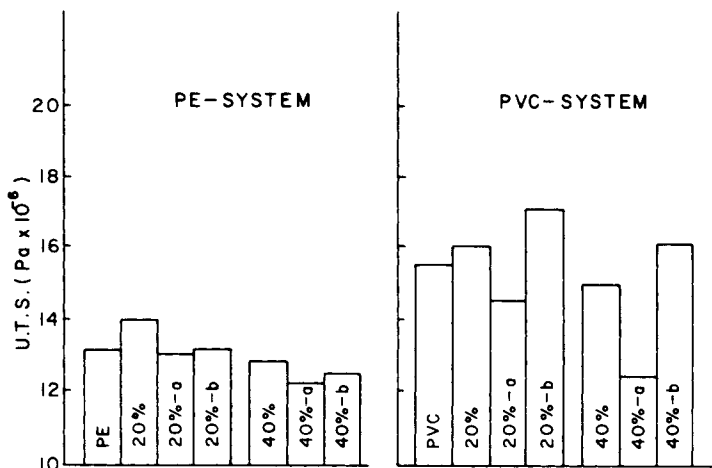
Fig. 3. Effect of filler/polymer interactions on the ultimate tensile strength of PE/CaCO$_3$ and PVC/CaCO$_3$.

The results shown in Figures 3 and 4 represent a transient state of mechanical responses for these compounds, since it is probable that under altered preparation procedures different sets of performance parameters would be generated.[15] Time-dependent changes in mechanical responses may be expected, therefore, and it was of interest to question whether or not the different interfacial force balances in these compounds would influence their aging behavior. The experimental sequences of aging at 70°C for PE and 100°C for PVC-based samples, described in the Experimental section, led to results which are summarized in Figures 5 and 6. No experimentally significant differences in behavior were noted between stocks with 20 wt % and 40 wt % fillers, when data were expressed in terms of percent property retention; the results for 40% loading, given in Figures 5 and 6, therefore, are typical of all data accumulated.
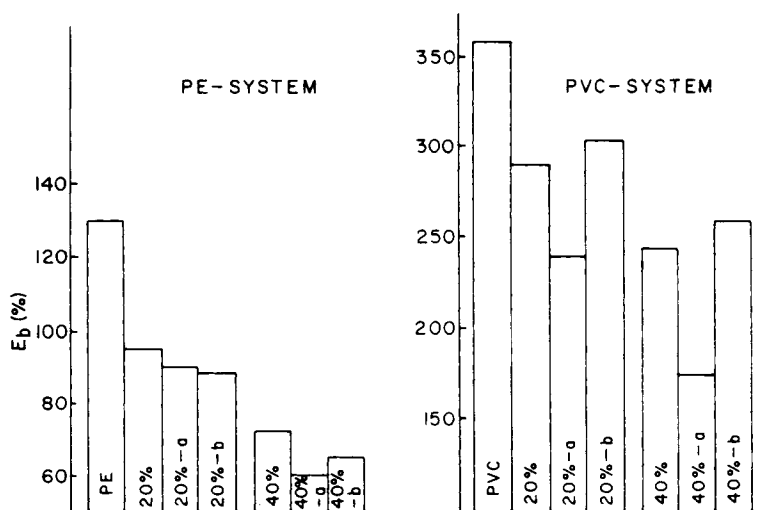

Fig. 4. Effect of filler/polymer interactions on the elongation at break of PE/CaCO$_3$ and PVC/CaCO$_3$.
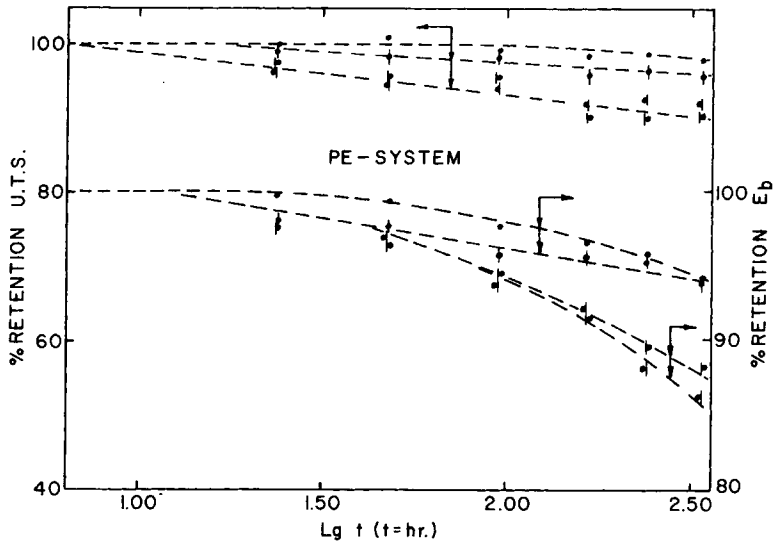
Fig. 5. Retention of ultimate tensiles and elongation properties on accelerated aging of PE/CaCO$_3$ compounds: (●) Unfilled PE; (◆) CaCO$_3$ (40%); (◖)(CaCO$_3$-a (40%), (◗) CaCO] $_3$-b (40%).

The aging characteristics of PVC stocks (Fig. 6) once again demonstrate a significant dependence on the condition of the polymer/filler interface.   We presume that the strongest bonding corresponding to the maximum $\Delta\Omega$ and involving CaCO$_3$-b is responsible for the stability of these compositions, while polymer containing CaCO$_3$-a ages most rapidly in terms of elongation loss and the slight gain in UTS.   The cause for property changes may be due, in appreciable part, to the rate of plasticizer migration to the sample surface and its subsequent volatilization.   The inherent tendency for DOP loss, demonstrated by the unfilled PVC control, reduces elongation but raises the tensile strength
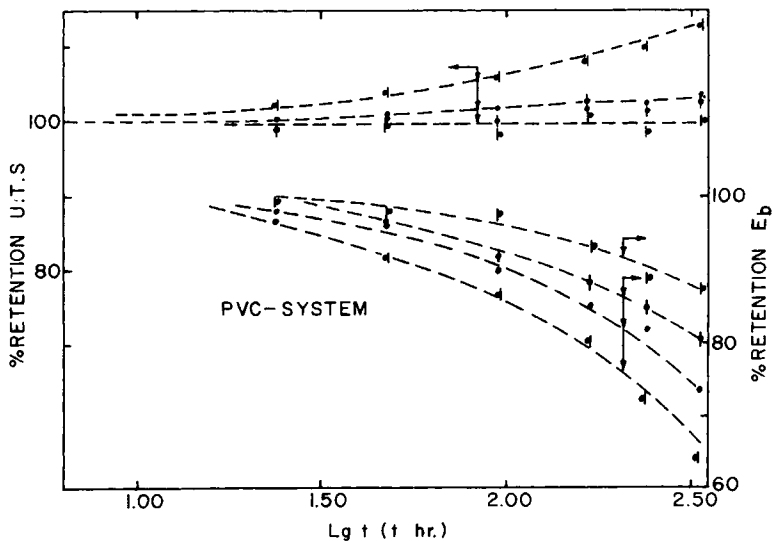

Fig. 6. Retention of ultimate tensiles and elongation properties on accelerated aging of PVC/CaCO$_3$ compounds: (●) Unfilled PVC; (◆) CaCO$_3$ (40%); (◖) CaCO$_3$-a (40%); (●) CaCO$_3$-b (40%).

at failure. We postulate that the addition of filler modifies the diffusion and volatilization tendencies of the plasticizer. The strong interaction of polymer and CaCO$_3$-b, and to a lesser extent between PVC and unmodified CaCO$_3$, produces effective wetting and strong bonding and, in terms of this postulate, would reduce the incidence of microvoids in the bulk specimen which may act as pathways for plasticizer migration. On the other hand, poor wetting and bonding with CaCO$_3$-a would have the opposite effect, and would promote plasticizer loss, consistent with the observations of Figure 6.

The inherent changes in ultimate properties of PE matrix polymer again are slight and only mildly influenced by any of the fillers involved. Property changes here may also be due to volatilization losses, presumably of low molecular weight components in the weight distribution of the polymer. The data are again consistent with an ease-of-migration hypothesis, the sequence of E_b and UTS changes following exactly the interaction guidelines suggested earlier. Again, therefore, no advantage is gained by introducing stronger electrostatic surface groupings in the filler surface, when that solid is to interact with a nonpolar matrix. In terms of the $\Delta\Omega$ parameter introduced above, the mechanical properties and their durability are correlated qualitatively; as with mixing parameters, property optimization in the PVC stocks is consistent with maximum values of $\Delta\Omega$. In the nonpolar polymer $\Delta\Omega \rightarrow 0$ is the apparent guideline to the choice of filler surface properties leading to effective dispersion, mechanical properties of the composite, and property durability.

CONCLUSIONS

Study of CaCO$_3$-filled PVC and PE compounds has shown that interactions at the polymer–filler interface exert a significant influence on the ease-of-dispersion and on the mechanical properties as well as their durability in the filled compounds.

Polymer–filler interactions have been characterized by their respective capabilities for the retention of acidic, basic, or neutral vapor probes in IGC experiments. The IGC route has been used successfully to apply acid/base interaction concepts to polymer/filler pairs and empirical interrelationships appear to link the interaction concepts with mixing performance and with mechanical properties at large deformation of the resulting solids.

Microwave-plasma polymerization procedures have been used to modify the surface properties of CaCO$_3$; it has been shown that acidic or basic surface properties can be designed into such fillers by the plasma process, depending on the choice of monomer gas. Acid/base concepts have also been used in the selection of these monomers. The plasma route appears to represent a powerful experimental tool for the tailoring of desired property balances into multicomponent polymer systems.

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