

# Property Stabilization in Filled, Drawn Polyethylene

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## SYNOPSIS

Mechanical properties of high density polyethylene (HDPE) extended to draw ratios in the 20–40 range have been determined and compared with corresponding properties of the polymers containing particulates including rutile, carbon black, iron oxide, and mica. Shrinkage of drawn structures was studied to temperatures near the fusion of the polymer host. The degree of interaction at polymer/additive interfaces was varied by surface coating certain of the solids with standard coupling agents. Solids were found to increase tensile moduli and to decrease shrinkage, particularly at higher exposure temperatures. The magnitude of changes due to the presence of solids was shown to depend on the apparent interaction at contacts between host and additive. In a dispersion–force matrix, like HDPE, benefits were optimized when the particulates were amphoteric or neutral, rather than having pronounced acid or base interaction potentials.

## INTRODUCTION

The importance of the interface to the properties of multicomponent polymer systems is manifest, as illustrated by many current reports, including several from our laboratories.<sup>1–3</sup> Additives to a polymer matrix such as fibers or fillers may make diverse contributions to the mechanical properties of the polymer and, where pertinent, the different contributions may be rationalized by considering the specific, or acid/base forces acting at interfaces between matrix and additive. The present paper considers specified properties of filled polyolefin structures, notably those based on a linear, high density polyethylene (HDPE). Emphasis is on the apparent contribution of interfacial phenomena to the drawability of the filled polymer and to shrinkage when the drawn structures are exposed to elevated temperatures.

There is intense interest in the formation of polyolefin structures with high mechanical strength. Various routes are known for elevating the modulus of HDPE from the < 1 GPa range, common for articles produced by standard extrusion, molding op-

erations, etc. to values well in excess of 100 GPa. One such route involves gel spinning of polyolefin fibers, the subject of a copious literature.<sup>4,5</sup> High modulus structures also may be obtained by conventional melt extrusion, provided that measures are taken to elevate the draw ratio (DR) of the polymer from the usual range of less than 10 to 20 or more. Examples of this route also abound.<sup>6,7</sup> The published literature strongly implies that high DR values, and consequently high polymer strength, is associated with control over the entanglement state of the polymer at the time of processing and orientation. By way of confirmation, we have shown recently<sup>8</sup> that solution/precipitation steps reduce the entanglement density of HDPE (and of other thermoplastic polymers). When these materials are processed and oriented, additional chain disentanglement can take place more easily and higher DRs are attained than in unmodified, control polymers. Ultradrawn HDPE structures also have been produced by extruding HDPE/wax blends.<sup>9</sup> In the process, the wax acts as diluent, and facilitates the disentanglement of polymer chains during processing operations.

The morphology of high modulus HDPE structures differs substantially from that of articles produced by conventional means.<sup>10–12</sup> The character-

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istics of drawn, high-modulus HDPE arise from stacks of oriented lamellae, coincident with the draw direction, the thickness of which depends on the draw temperature. This contrasts with the conventional polymer solid, marked by unoriented lamellar crystallites, whose thickness is determined by the crystallization temperature. The oriented structures are thermally unstable, however. As the temperature increases toward the melting range of the polymer, entropic and elastic relaxation forces promote disorientation and shrinkage which reverts properties to those of conventionally produced solids.<sup>13</sup> The obvious importance of shrinkage to the utility of drawn HDPE has led to numerous studies of the phenomenon.<sup>14-16</sup> Property loss through shrinkage is initiated, in all likelihood, by the plasticizing effect of amorphous moieties present in the drawn structure. This draws attention to interfacial effects, since an immobilization of these amorphous portions at the surface of suitably chosen solid additives may be beneficial to the retention of high moduli and mechanical strength at high temperatures.

In accordance with the above considerations, we report on the drawing and shrinkage behavior of HDPE filled with rutile, mica, carbon black, and iron oxide particles. The fillers were used as received, and in certain cases following surface modification by silane and titanate coupling agents. The technique of inverse gas chromatography (IGC)<sup>17</sup> was used to determine the acid/base interaction potential of fillers and polymer host, and the corresponding dispersion surface energies. The inherent dispersibility of the particulates was measured by a rheological method.<sup>2</sup> In this manner it is possible to estimate the contribution of interfacial phenomena to property enhancement in an important class of polymer structures.

## EXPERIMENTAL

### Materials

The host polymer was a high density, linear PE (HDPE), supplied by Union Carbide Corp. It had a density of 955 kg/m<sup>3</sup>. Size exclusion chromatography, with trichlorobenzene at 135°C as solvent, gave molecular weights as follows:

$$M_n = 93,100, M_w = 680,000, \text{ and } M_z = 822,000$$

The fillers included three different, surface-coated rutiles (TiO<sub>2</sub>) from Tioxide Canada, Inc., with surface areas  $A = 9 \pm 1 \text{ m}^2/\text{g}$ ; a reagent grade iron

oxide (Analar,  $A = 3.5 \text{ m}^2/\text{g}$ ); a carbon black from Cabot Carbon Inc., ( $A \sim 90 \text{ m}^2/\text{g}$ ), and Suzorite platelet mica.

The surfaces of these solids were modified in certain cases by treatments with amino propyl triethoxy silane (A-100, Union Carbide Inc.), or with a pyrophosphatotitanate (CAPOW L12/H, Kenrich Petrochemical Inc.). For silane treatments, dilute silane solutions in methanol/water (90/10), adjusted to pH 5 by the addition of acetic acid, were contacted with fillers in proportions of 2 g silane to 100 g filler. Following 15 min hydrolysis time and 10 min contact with the filler, the solids were recovered and oven-dried (110°C, 24 h) for further use. The titanate agent was added directly to the matrix polymer at the time of compounding.

### Methods

Samples containing up to 20 wt % filler were prepared by roll-milling at 190°C, using the Babender Plasticorder. The roll mill gap was 2 mm, and the roll speed was set at 30 rpm, corresponding to a torque output of 400 N m. Thermal stabilizer at 0.1 wt % of polymer was added at the compounding stage. Milled stocks were granulated, then compression molded (40 MPa, 165°C), and slow-cooled to room temperature in the press. The plates were used to cut dumbbell samples, 27 × 5 mm, which were then drawn on an Instron test machine fitted with an environmental chamber. This allowed draw experiments to be conducted at temperatures to 125°C. The tensile properties of the compounds also were measured with the Instron tester. Throughout these procedures the drawing rate was kept constant at 10 mm/min. Drawn specimens were exposed to elevated constant temperatures in air ovens, and shrinkage was determined from changes in the distance between previously applied ink marks. All DR, tensile property and shrinkage data were repeated at least three times; the results reported below carry uncertainties not exceeding 10%.

The surface characteristics of the fillers, except the mica, were determined by the methods of inverse gas chromatography (IGC). These applied developments recently reported by Schultz and co-workers<sup>18</sup> and by one of us<sup>3</sup> to obtain acid/base interaction indexes for the solids. The procedure calls for using the solids as stationary phases in experiments where first alkane vapor probes and then reference acid and base vapors are used to contact the solids. Reference acid and base vapors, chloroform (chl) and tetrahydrofuran (thf), respectively, were chosen from Gutmann's tabulations<sup>19</sup> of electron

acceptors and donors. In IGC analyses, retention volumes per unit area of the solids,  $V_n$ , were expressed as functions of the cross-sectional area of the vapor molecules,  $a$ , and their dispersion-force surface energies,  $\gamma_l^d$ , according to<sup>3,18</sup>

$$RT \ln V_n = 2Na(\gamma_l^d)^{1/2}(\gamma_s^d)^{1/2} + c \quad (1)$$

where  $\gamma_s^d$  is the dispersion-force surface energy of the solid,  $N$  is the Avogadro number, and  $c$  is a constant. As called for by eq. (1), this led to linear relationships when alkane vapors were used as probes, and thus to evaluations of the dispersion-force surface energies. Deviations from these straight lines for the retention of chl and thf were used to define acceptor and donor numbers (AN and DN) of the solids.<sup>3</sup> An overall interaction parameter,  $K_i$ , defined as

$$K_i = DN - AN \dots \quad (2)$$

also was calculated. Negative values of  $K_i$  designate an acidic substance, positive values a base, and amphoteric or neutral solids report a zero value of the parameter. In amphoteric solids the null reading is due to a balance of acid and base numbers ( $AN \sim DN$ ), while for neutral solids  $AN = DN = 0$ .

Values of  $K_i$  are given in Table I along with the solids' surface energies. Also given in the table are the inherent agglomeration indexes,  $C$ , as measured by the powder rheological method described in Ref. 2. Increasing values of  $C$  denote powders with inherently stronger agglomeration tendencies. Clearly, the rutiles represent the three major interaction categories, R-1 being amphoteric, R-2 a base, and R-3 a mild acid. The carbon is a strong acid; the iron oxide a mild base. Substantial differences exist among the dispersion surface energies of these solids, but all are greater than that for the host PE. Generally, the selected fillers may be rated as readily dispersible, with  $C$  values below about 300; only R-

2 suggests moderate agglomeration. This pigment would require higher shear energies for full dispersion in a given matrix than would similar basic solids with lower  $C$  indexes.

## RESULTS AND DISCUSSION

### Mechanical Property Parameters: Modulus

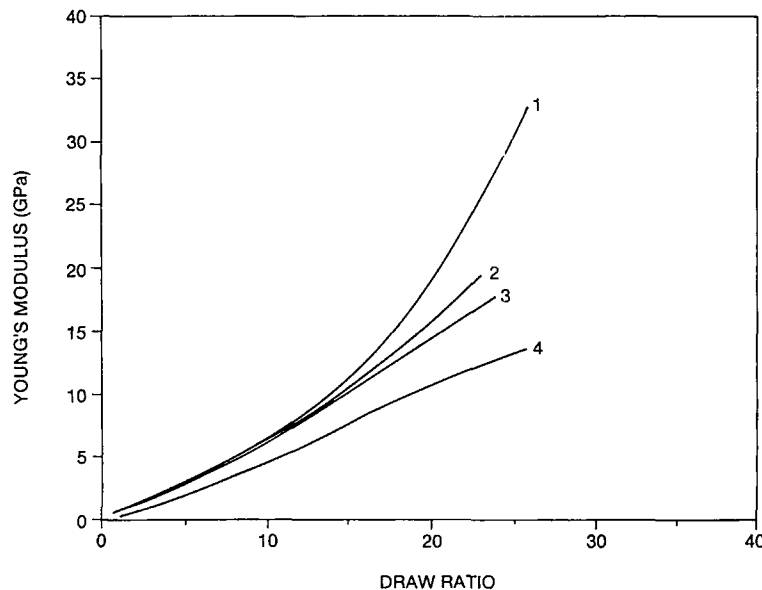
The drawability of HDPE depends critically on the draw temperature, optimum results being obtained near the beginning of the polymer's melting range. For the present polymer, temperatures in the 110–120°C were found to be preferred, and the following discussion pertains to specimens drawn in this interval. The contribution of fillers to the drawability and the modulus of HDPE is illustrated in Figures 1 and 2. In the first of these are shown the modulus/DR relationships for unfilled and rutile-filled version of the polymer. As expected, the modulus of HDPE rises significantly in the oriented polymer, attaining a value of about 14 GPa at break, corresponding to a DR near 26. The presence of rigid particles further raises the modulus, the effect being appreciable even at the relatively low loading level illustrated, and in excess of expectations based on prevailing theories. Less expected is the difference among the three rutile-containing materials. This difference is not manifested in samples oriented to DR less than about 10, but becomes increasingly evident at higher DR. Rutiles 2 and 3 raise the modulus near rupture into the 20 GPa range, but at the sacrifice of some drawability. Rutile 1, however, produces compounds that can be drawn to DR near 30, and attain moduli well in excess of 30 GPa. The contribution of interfacial effects, due to differences in the surface properties of the three fillers, is implied.

Figure 2 provides a broader overview of the performance of filled HDPE, again at the 0.5 vol % loading level. Again there is strong inference that interfacial effects at polymer/filler contacts play

**Table I Surface Parameters for Fillers Used in This Study<sup>a</sup>**

Solid	$K_i$	Description	$\gamma_s^d$ (mJ m <sup>-2</sup> )	$C$	Description
Rutile 1	-0.3	Amphipatic	50.7	280	Light agglom.
Rutile 2	1.7	Base	45.4	550	Moder. agglom.
Rutile 3	-1.1	Mild acid	46.7	190	Light agglom.
Iron oxide	0.9	Mild base	46.2	150	Nonagglom.
C black	-3.6	Acid	39.8	210	Light agglom.

<sup>a</sup> Note:  $\gamma_s^d$  of PE = 29.8 mJ m<sup>-2</sup>.

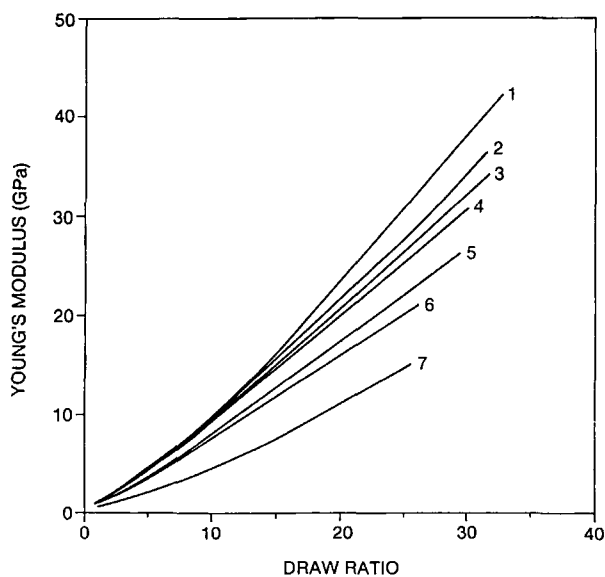


**Figure 1** Modulus–draw ratio variations for rutile-filled HDPE; 0.5 vol % filler level, draw  $T = 115^{\circ}\text{C}$ : (1) R-1; (2) R-2; (3) R-3.

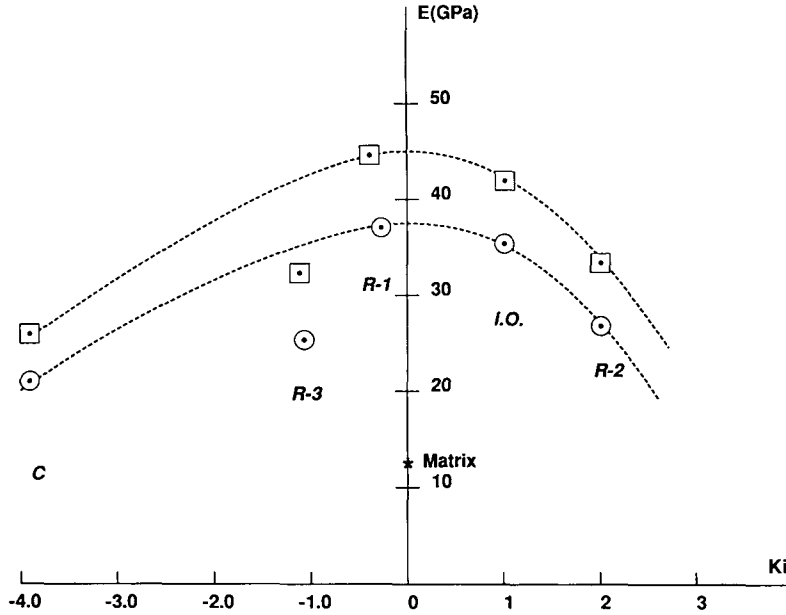
important parts in determining the measured property. Rutile 1, particularly when silane-modified, provides the best balance of drawability and modulus. Titanate-modified compounds were found to be only marginally effective in the present study.

The predominance of distinctive filler effects at higher DR suggests that wetting or adhesion at

polymer/filler contacts is involved. It may be argued that drawing generates internal stresses leading to failure at points of stress concentration. Weak polymer/filler interfaces would be logical loci for such stress effects. Judging from the results, pronounced acidity or basicity of the filler surface is detrimental to interfacial strength, when the matrix can interact through dispersion forces alone. The pattern of results shown in Figure 3 amplifies on this. Here the modulus for specimens drawn to DR 22 at  $110^{\circ}\text{C}$ , and containing 0.5 and 5 vol % filler, is plotted vs. the acid/base interaction number  $K_i$  of the filler. The amphoteric R-1 generates compounds with a clearly discerned maximum in modulus. Fillers more strongly imbalanced toward electron donor or acceptor capability produce lower moduli, although in all cases they exceed the modulus of the unfilled control sample. This form of data representation, although confirming interfacial contributions, is flawed: For example, it cannot account for the predominance of the amphoteric R-1 over the competing versions of this pigment. It does not explain the apparently consistent failure of R-3 to lie on the smooth curve joining other data points, and it provides no clear reason why the modulus should decrease more rapidly for compounds with basic rather than acidic fillers. It is possible that acid/base interactions play subordinate roles in the definition of interfacial conditions in these HDPE compounds. Alternative considerations, founded on dispersion-force surface energies, may be more pertinent, and will be discussed later in this paper.



**Figure 2** Modulus–draw ratio variation for filled HDPE; 0.5 vol % filler, draw  $T = 115^{\circ}\text{C}$ : (1) R-1, silane mod; (2) R-1; (3) C, titanate mod.; (4) C; (5) mica, titanate mod; (6) mica; (7) unfilled.

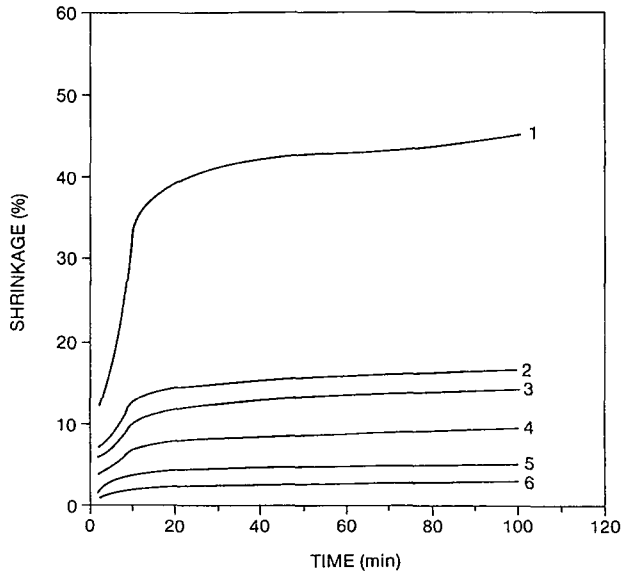


**Figure 3** Young modulus (30°C) vs. acid/base interaction number of fillers; samples drawn to DR = 20, at 110°C: (O) 0.5 vol % filler; (□) 5.0 vol % filler.

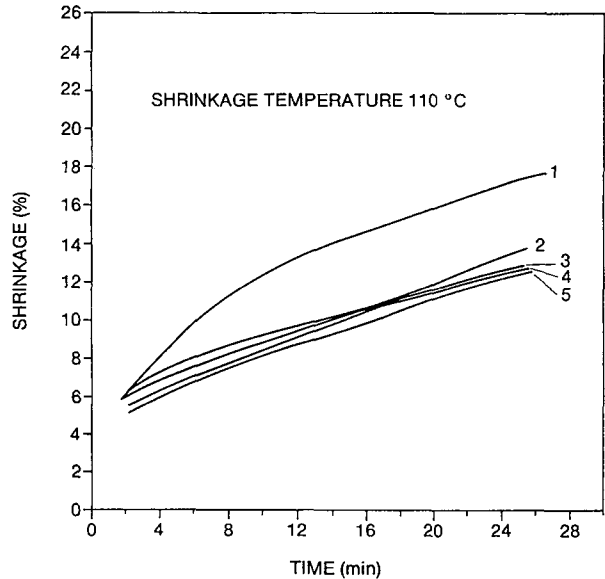
**Shrinkage**

As noted already, in applications of high-strength HDPE structures, there is concern over the temperature range in which the materials may be used without undue loss of desirable properties. The problem is illustrated clearly in Figure 4, by the shrinkage behavior of unfilled HDPE, drawn to an

initial DR = 20 at 110°C, and then exposed to elevated temperatures, as indicated. Measurable dimensional changes occur at temperatures as low as 95°C, well below the crystallization range of the polymer. As that range is approached and entered, the shrinkage becomes pronounced, attaining major importance at and above 110°C. Shrinkage phenomena have been studied extensively, notably by



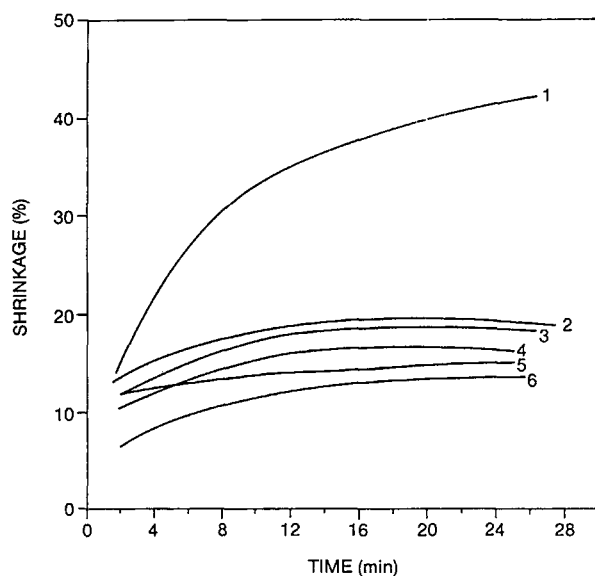
**Figure 4** Shrinkage rates of filled HDPE; drawn to DR = 20 at 110°C: (1) 125°C; (2) 115°C; (3) 110°C; (4) 105°C; (5) 100°C; (6) 95°C.



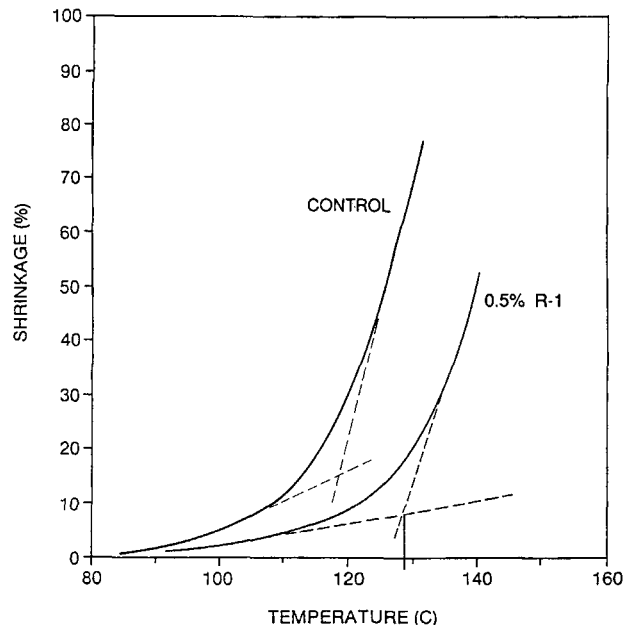
**Figure 5** Shrinkage of filled HDPE drawn to DR = 20 at 110°C; filler level at 0.5 vol %: (1) unfilled; (2) mica; (3) iron oxide; (4) C; (5) R-1.

Peterlin and co-workers,<sup>20-22</sup> who related the effect to a loss of orientation in the amorphous fraction of the polymer, with the consequent loss of two or more decades in the elastic modulus of these portions. To the extent that additives may stabilize the oriented, amorphous chain molecules, or effect a nucleation leading to higher crystallinities, they should reduce shrinkage effects.

The results shown in Figure 5 for compounds with various of the fillers exposed to 110°C are in keeping with expectations. The abscissa here is restricted to 30 min to focus on the dimensional changes occurring in early, critical exposure periods. Each of the fillers reduces shrinkage losses, even at the low loadings selected for examination. As was the case with modulus changes, shrinkage effects vary from filler to filler, with the mica least effective, and rutile R-1 best able to limit shrinkage. However, the differences between iron oxide, carbon, and the rutile filler are slight. A broader overview of the situation again is presented, this in the form of Figure 6. Included here are comparisons illustrating the contribution of coupling agents. These, of course, are intended to enhance bonding at the polymer/filler interface. In terms of the proposed mechanisms for shrinkage,<sup>20-22</sup> their presence should therefore further limit shrinkage under constant conditions of comparison. In general, the expectation is met, although the magnitude of contributions due to the



**Figure 6** Shrinkage of filled HDPE drawn to DR = 20 at 110°C; shrinkage  $T = 110^{\circ}\text{C}$ ; all fillers at 0.5 vol % level: (1) unfilled; (2) iron oxide, titanate mod; (3) C; (4) C, silane mod.; (5) R-1, silane mod; (6) R-1.



**Figure 7** Isochronous shrinkage (10 min) of unfilled and R-1-filled HDPE from initial DR = 20.

use of coupling agents is slight, more particularly when the titanate is employed.

A useful index for the effectiveness of fillers as promoters of thermal stability in drawn HDPE may be obtained from isochronous cuts through representations such as those of Figure 4. The procedure is illustrated in Figure 7; here we compare the shrinkage vs. temperature behavior of the control HDPE and its rutile-containing version, in a 20 min exposure period. The curves are very similar, except for a distinct displacement in the temperature axis of the curve for HDPE containing R-1. An empirical parameter may be defined from relationships of the type shown. This is indicated by the construction in the figure. The intersection of rapid and initial, slow shrinkage losses is used to define a critical temperature for accelerated shrinkage,  $T_c$ . That temperature has been increased by the presence of rutile R-1 from 118°C for the unfilled control polymer to 129°C for the filled version.

A summary of  $T_c$  values is given in Table II. The tabulation is restricted to systems containing 0.5 vol % filler, exposed for 10 min to high temperatures. Larger quantities of filler, however, do not change the situation appreciably, so that the reported data provide an adequate overview of the contributions made by these solids to the thermal stability of drawn structures. Further, no significant change in  $T_c$  values is obtained when the isochronous cuts are made at any point in the 5–30 min interval. The

**Table II**  $T_{crit}$  for Accelerated Shrinkage: 10 min Exposure Time<sup>a</sup>

Sample	$T_{crit}$ (°C)
Control PE	118
PE + R-1	129
+ R-1 silane	131
+ R-1 titanate	126
+ R-2	122
+ R-3	124
+ Iron oxide	125
+ Carbon black	126

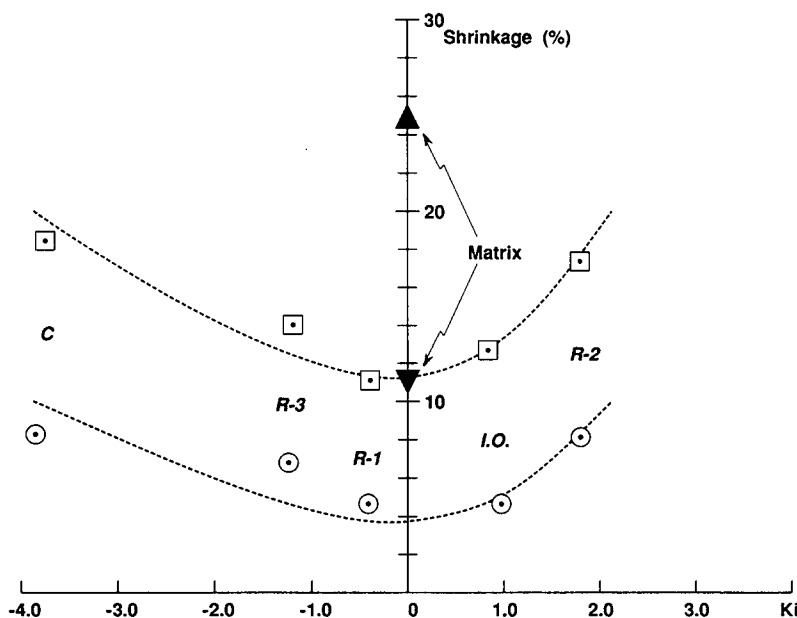
<sup>a</sup> All compounds contain 0.5 vol % filler.

results are in good, qualitative accord with the perceived state of interfacial bonding between host and the various fillers. Again the amphoteric rutile performs best among the chosen fillers. The coupling agents make relatively minor contributions; the silane increases thermal stability somewhat when coupled with R-1, while the titanate actually lowers  $T_c$  by some 5°C. We may conclude, however, that the use of fillers, with or without the concurrent use of coupling agents, represents a reasonable strategy for increasing the use temperature of drawn HDPE, preference being given to fillers with balanced acid/base characteristics.

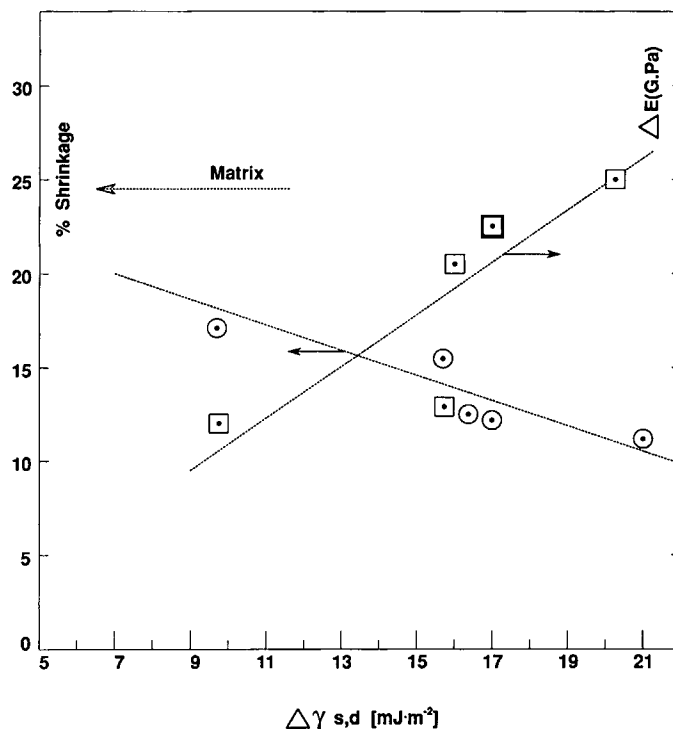
The latter point is confirmed by Figure 8, an analogy to the modulus representation of Figure 3.

Shrinkage for 20 min exposures to 100 and 115°C is used to illustrate the variation of shrinkage with the acid/base interaction potential of the fillers. This time a shallow minimum is obtained for the amphoteric R-1, while lesser reductions of shrinkage are noted on using fillers with either more pronounced acid or base properties. As in the earlier case (Fig. 3), however, acid/base interactions may not be the only or indeed the most reasonable driving forces for the observed mechanical property responses. The quality of interfacial wetting at polymer/filler contacts may be a prime consideration, and this may be expressed by the difference between dispersion-force surface energies of the participating materials. Assuming that the wetting process occurs during high temperature compounding, the relevant correlating parameter would be the difference between dispersion-force surface energies,  $\Delta\gamma_s^d$ , of filler and polymer at that temperature. These values are presently unavailable but data obtained from the IGC investigations may serve as reasonable approximations.

The correlating capability of  $\Delta\gamma_s^d$  is shown in Figure 9. Clearly the modulus increment in samples drawn to DR = 25 at 110°C, as well as shrinkage (at 115°C for samples drawn to DR = 20), correlates strongly with differences in the dispersion surface energies of filler and polymer. Only the modulus datum for samples using R-2 fails to fall on a line for which, otherwise, linear regression generates a cor-



**Figure 8** Isochronous shrinkage (20 min) of filled HDPE as function of acid/base interactions; initial DR = 20 at 100°C: (○) 100°C exposure; (□) 115°C exposure.



**Figure 9** Modulus increment and shrinkage in filled HDPE: Dependence on dispersive surface energy parameter. Shown is 20 min shrinkage at 115°C (from DR = 20), and modulus rise at DR = 20.

relation coefficient of 0.984. It is possible that the relatively high agglomeration index for R-2 (see Table I) prevents this pigment from being as fully dispersed by present compounding methods as other solids, accounting for the observation. A similar, high coefficient (0.980) applies to the shrinkage relationship. These correlations are stronger than the corresponding ones based on the use of acid/base parameters. Evidently, with the matrix chosen for this work, interfacial wetting is a determining factor for the eventual strength of polymer/filler bond strength, and for possible crystal nucleation. It is a key variable therefore in the development of modulus in drawn, filled HDPE. Similarly, enhanced high temperature tolerance may be produced in high-strength HDPE structures through control over interfacial wetting phenomena.

## CONCLUSION

The present work has shown that:

- IGC techniques may be applied usefully for the determination of dispersion surface energies and of acid/base interaction potentials in components of filled polymer systems.

- The use of particulates can increase the initial modulus of drawn HDPE. Values in the vicinity of 30 GPa can be attained when the filler is not strongly acidic or basic.
- Shrinkage of drawn HDPE is reduced by the incorporation of fillers, the magnitude of the effect depending on the strength of the polymer/filler interface.
- Increases in the moduli of drawn, filled HDPE and decreases in the shrinkage of drawn structures at elevated temperatures have been shown to correlate with interfacial wetting, as expressed best by differences between the dispersion surface energies of fillers and host polymer. Lesser but useful correlations may also be drawn between mechanical performance parameters and the acid/base potentials of fillers.
- For dispersion-force polymer hosts such as HDPE, amphoteric, and, by inference, neutral fillers seem best suited for the generation of desirable modulus and shrinkage effects.

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