Surface Modification Strategies for Multicomponent Polymer Systems. III: Effect of Diblock Copolymer-Modified Rutile on the Morphology and Mechanical Properties of LLDPE/PVC Blends

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ABSTRACT: Rutile pigment was surface-modified by the adsorption of various diblock copolymers and used as a component in two- and three-component polymer blends involving the incompatible pair of linear, low-density polyethylene (LLDPE) and poly-(vinyl chloride) (PVC). Stress–strain analyses and electron microscopy show that the copolymer tethered to the rutile surface affects both mechanical and morphological properties of the blends. Inverse gas chromatography was used to evaluate dispersion surface energies and acid–base interaction parameters of the various solids. The mechanical and morphological characteristics of the blends can be rationalized by the concepts of acid–base and dispersion–force interaction. Of the copolymer modifiers used, the diblock based on polyisoprene and poly(4-vinyl pyridine) (PIP-P4VP) was best suited for use in LLDPE/PVC blends, ostensibly because of strong acid–base interaction between PVC and P4VP and mechanical interlocking between LLDPE and the PIP moiety. The properties of ternary blends were shown to be dependent on the method used for mixing the components. All mixing procedures used here resulted in time-dependent variations of mechanical properties, suggesting that none gave rise to equilibrium morphology in the compounds. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1891–1901, 2001

Key words: PVC; LLDPE blending; rutile; block copolymers; surface modification

INTRODUCTION

This article contributes to a series of communications[1–3] concerned with surface modification strategies for components of complex polymer systems, with the aim of identifying modification approaches beneficial to property development in the systems. Apparently an important concern,

therefore, is the control of interfaces and interphases separating the entities of the systems. The characteristics of interfacial regions are the subject of much current attention. As an example, their control through the addition of modifying agents such as silanes[4] may be viewed as a classical approach to the challenge. Recent work in our laboratories has shown[5] that electron donor–acceptor (acid–base) mechanisms may be responsible for the creation of morphologically uniform (isotropic) or nonuniform (nonisotropic) interphases, the former appearing to be better suited to the retention of mechanical properties under

accelerated aging conditions in filled polymer blends. Elsewhere,[6,7] the concept of smart polymers was advanced as a means for interphase control. Involved are specifically designed bifunctional polymers able to key into incompatible polymer matrix pairs. Acid–base exchanges may also be a factor in this technology. Grafting polymer moieties onto polymer, fiber, and filler surfaces is yet another approach to benefiting property development in multicomponent polymer systems. Among the methods recently reported for the production of polymer grafts are Ranby's photografting processes [8] and the use of corona discharges to activate surfaces for subsequent graft polymerization. An example of the latter was given in ref. 2, where rutile TiO$_2$ surfaces were activated by these discharges for the subsequent deposition of acrylic graft moieties.

The present communication reflects our continuing interest in the use of surface-modified particulates to promote compatibility in polymer blends. The use of fillers and pigments for the purpose was proposed on many occasions.[9,10] Lipatov and coworkers [11] have shown that the introduction of suitable fillers enhances the thermodynamic compatibility of binary polyethylene–polyurethane blends. Kalfoglon[12] used a variety of fillers in the compatible polyurethane–poly(vinyl chloride) PVC system, citing acid–base mechanisms to account for the morphology of the polymer–polymer interface. In an earlier report,[1] we made use of diblock polymers to modify the surfaces of rutile, so as to confer either acidic or basic characteristics to the pigment surfaces. The feasibility to tether such polymers onto the rutile raised interest in the potential usefulness of the modified pigments as bridging agents in inherently immiscible binary polymer systems, a possibility explored in the present work.

The immiscible polymers selected in this instance were linear, low-density polyethylene and poly(vinyl chloride) (LLDPE/PVC). Reported are the effect of adding the pigments on the mechanical and morphological properties of the individual polymers and their blends, and acid–base interaction parameters for the rutile–polymer combinations. Acid–base interactions are applied toward a rationalization of observed property changes. Finally, in some instances, mechanical and morphological properties are reported for blends prepared by different mixing sequences. The partitioning of pigment particles between the matrix polymers may be expected to reflect the different thermodynamic interactions within the system. A given mixing procedure, therefore, may not necessarily lead to equilibrium partitioning, so that the detail of mixing protocols may be a variable in the properties displayed by the system. The reported results elaborate on the expectation.

EXPERIMENTAL

Materials

The rutile (designated as R), in its original and surface-modified versions, was that described in ref. 1, in which also were given details on the surface-coating procedures. Briefly, the pigment as obtained was a dry powder with a nitrogen adsorption (BET) surface area of 10 m^2/g. It was used as received, in noncoated form, and also as modified by tethering onto the surface the following diblock copolymers (codes and number-average molar masses in parentheses):

polystyrene–poly(4-vinyl pyridine) (PS–P4VP; M_n = 63,000)

polystyrene–poly(acrylic acid) (PS–PAA; M_n = 140,000)

polyisoprene–poly(4-vinyl pyridine) (PIP–P4VP; M_n = 70,000)

silyl–hydroxyl-terminated polystyrene (PS–SiOH; M_n = 29,000)

Details of copolymer synthesis were given elsewhere,[13–15] as were results of studies[16] in which the copolymers were used as additives to two-component LLDPE/PVC blends. The pigment coating procedure, as specified in ref. [1], results in complete coverage of the rutile surface, documented by X-ray photoelectron spectroscopy (XPS) analyses. However, because the strength of the copolymer–rutile bond may vary because of surface heterogeneity in the pigment substrate, loosely held copolymer was extracted from the coated solid by Soxhlet extraction, using tetrahydrofuran (THF) as fluid. Soxhlet treatment was of 4 h duration, sufficient to bring the coated pigments to invariant weight.

The LLDPE was supplied by Union Carbide Chemicals and Plastics Co. (Bound Brook, NJ) and identified as HS-7028 Nature 7. Its melt flow index was 1.0 g/min and its melting peak was 125.5°C, as measured by DSC. The PVC, supplied by Synergistic Chemicals Inc., was a commer-

cially marketed sample with $M_w = 54,000$. It contained 7 phr of methyltin thermal stabilizer.

Blending

Two-component polymer–pigment and three-component systems were investigated. In all cases, a Brabender mixer was used. For two-component PVC/R systems, the mixer chamber was charged with PVC and allowed to equilibrate at 175°C. Rutile was then added to produce 13 and 20 wt % compounds and mixed for 5 min at a rotor speed of 50 rpm. A similar procedure was followed in preparing LLDPE/R blends. Three-component systems were based on LLDPE/PVC blends containing 25 wt % PVC. However, because of the pigment partitioning considerations noted above, four distinct blending procedures were followed.

Procedure A. The chamber was charged with PVC and the polymer equilibrated, as above. The rutile was then added and mixed for 5 min, whereupon the LLDPE component was added and mixed for an additional 5 min.

Procedure B. This procedure followed the above mixing temperature, time, and rotor speed values, but reversed the initial polymer–pigment contact by first charging the chamber with LLDPE and allowing that polymer to equilibrate at 175°C. The rutile was introduced next and mixed, and finally the PVC was added and blended into the compound.

Procedure C. The chamber was charged with the polyethylene and upon gelling, the PVC was added and blended for 5 min. Rutile was added to the polymer mixture and again blended for an additional 5 min. This procedure is referred to as the standard procedure

Procedure D. All three constituents of the blend were introduced simultaneously into the mixing chamber. Following attainment of thermal equilibrium, the components were mixed for 10 min.

In all cases, compounded materials were compression molded in a Carver Press at 180°C for 5 min and quenched in cold running water.

Mechanical Properties

An Instron Table Model tester, operating at 26°C, was used for the evaluation of blend mechanical properties. The crosshead speed was set at 1 mm/ min for modulus determinations and at 10 mm/ min for stress–strain measurements. Reported results are averages of eight determinations and carry an uncertainty of ±5%. In certain cases, impact-strength measurements were performed with an Izod Impact Tester, again at 26°C. Impact energies/unit section area as reported here are averages of eight determinations and carry an uncertainty of ±8%.

Morphology

The microstructure of blends was investigated by electron microscopy. Fracture surfaces were prepared cryogenically, by immersing compression-molded specimens in liquid nitrogen for 10–15 min. Fracture surfaces were coated with gold-palladium alloy prior to examination on a Jeol Model JSM-T200 scanning electron microscope.

Acid–Base Interaction Parameters

The procedures of inverse gas chromatography (IGC)[17–19] were followed to measure acid and base interaction constants, Ka and Kb, respectively, for polymers and the various rutile solids. Stationary phases were packed in previously washed and dried stainless steel columns and housed in a Varian 3400 gas chromatograph, equipped with hot wire and ionizing flame detectors. Retention volumes at infinite dilution of injected probes were measured in the range 30–80°C. Triplicate determinations were reproduced to better than 4% in all cases and used to obtain Ka, Kb, and the dispersive surface energy of the solids, γ_s^d, according to well-established procedures.[17–19] The vapor probes used in line with these procedures were the alkanes from nC6 to nC9, and diethyl ether, tetrahydrofuran, ethyl acetate, and chloroform. The polar set was chosen on the basis of their electron acceptor and donor numbers (AN, DN), as stated in Gutmann's theory of acids and bases.[20] Further details on ways in which the IGC data were used is found in the discussion section of this article.

RESULTS AND DISCUSSION

Effect on Filled Polymers of Tethering Diblocks onto Rutile Component

Attention is drawn first to the effect of adding unmodified and modified TiO_2 on the mechanical and morphological properties of the individual

Table I Mechanical Properties of LLDPE Compounds

	Modulus (MPa)			Yield Strength (MPa)		
Rutile load (wt %)	0	13	20	0	13	20
	52.8			7.7		
Rutile (R) unmod.		58.8	66.6		8.3	7.9
R/PS–P4VP		62.8	62.5		7.3	7.7
R/PIP–P4VP		64.5	68.3		8.8	9.0
R/PS–PAA		61.3	69.6		8.4	8.2
R/PS–SiOH		63.6	69.1		8.7	9.3

matrix polymers. The results of stress–strain analyses for LLDPE are summarized in Table I. As already noted, the materials were blended by procedure C. It was difficult to obtain reproducible data at ultimate failure of the compounds; thus, only moduli and yield strengths are reported. The presence of rutile raises the modulus of the polymer somewhat, and at the lower loading level of 13 wt % the effect is a little greater in the presence of the interface modifiers. Here R/PIP–P4VP and R/PS–SiOH are the preferred copolymer coatings. At the higher pigment loading, the variation in moduli for the various filled samples is very slight. Here, of course, the detailed morphology of the dispersed phase may play a more pronounced role. The yield strength of the compounds is a better indicator of interfacial states, because it is believed that the resistance to nonlinear deformation depends more strongly on microstructural factors, such as the particle size of the filler and its distribution in and interaction with the matrix. The physisorption of LLDPE on the high-energy rutile surface tends to strengthen the compound, and the effect is again more pronounced in the presence of PIP–P4VP and PS–SiOH modifiers. In the case of the PIP–P4VP, the presence of the rubber moiety may result in mechanical interlocking and thus stronger bonding with the nonpolar polyolefin host.

The results of stress–strain analysis for PVC compounds are stated in Table II. In these blends, properties at failure were accessible and, therefore, are stated in the table. As expected, the presence of rutile increases the polymer modulus, but lowers the yield strength, the yield point being observed at about 3% elongation. Ultimate strength and ductility also diminish in the presence of the pigment. The diblock modifiers at 13 wt % loading tend further to increase the modulus, but increasing the pigment concentration has no further significant effect. The PS–4VP and PS–SiOH copolymers are the preferred surface modifiers. These two were also found to shift the yield point to near the 12% elongation mark. Furthermore, although modifiers PS–PAA and PIP–P4VP produce significant lowering of the stress beyond the yield point, no such softening is observed with the PS–P4VP and PS–SiOH agents. Yielding may be interpreted as either a crazing or a dewetting phenomenon, lowering the strength of the matrix polymer/pigment interface, suggesting that the preferred copolymers generate interfaces not subject to this problem.

Table II Mechanical Properties of PVC Compounds

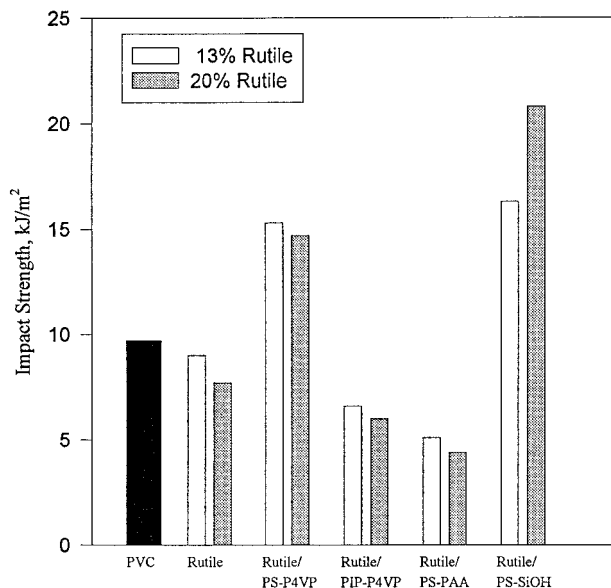|							Ultimate					
	Modulus (MPa)			Yield Strength (MPa)			Strength (MPa)			Elongation (%)		
Rutile load (wt %)	0	13	20	0	13	20	0	13	20	0	13	20
	370			11.7			47.4			22.8		
Rutile unmod.		430	460		8.9	10.0		41	37		17.7	17.9
R/PS–P4VP		490	490		8.7	11.3		35	28		16.2	17.2
R/PIP–P4VP		480	470		7.0	10.8		30	24		15.6	15.1
R/PS–PAA		450	460		5.2	8.0		44	36		16.0	14.5
R/PS–SiOH		490	480		9.7	9.9		40	39		19.3	21.4

Figure 1 The impact strength of PVC containing variously modified rutile pigment. All compounds prepared by mixing procedure C.

The impact resistance of PVC formulations is shown in Figure 1. The presence of rutile produces a slight decrease in the impact property, more noticeably so at the higher solids content. The tendency of rigid fillers to lower polymer impact resistance has long been recognized[21] and attributed to the particles acting as crack initiators. Cracks then propagate readily through a material such as rigid PVC. The trend toward augmented losses in impact resistance demonstrated by PIP–P4VP and PS–PAA modifiers suggests that these lead to greater degrees of agglomeration in the pigment. PS–P4VP, however, raises the impact property by some 35%. Stronger interfacial bonding and/or improved dispersion may be responsible. The increase in impact resistance produced by PS—SiOH-modified rutile is even more remarkable, the value being nearly tripled relative to that for unmodified rutile at the higher loading. Morphological factors would seem to be a likely explanation of this observation. Relevant scanning electron microscopic (SEM) images are presented in Figure 2(a,b). Shown are dispersions in the PVC matrix of unmodified rutile [Fig. 2(a)] and rutile coated by PS–SiOH. The quality of dispersion is superior in Figure 2(b), the ratio of average particle sizes in Figure 2(a) and (b) being in the range 3–4.5. An additional factor in the performance of compounds with the variously modified rutiles may be the degree of acid–base

interaction at interfaces. This is given further consideration later in this section of the article.

Three-Component Systems

A summary of the mechanical properties for these compounds is given in Table III. Throughout, the designated reference mixing procedure C was used to prepare the materials. The inherent incompatibility of the matrix polymers is clearly seen in the SEM image of Figure 3. Here the minor PVC phase forms large agglomerates, consistent with noninteracting interfaces. Acid–base considerations again enter the picture, PVC being a known acidic polymer, the polyolefin being a neutral one. Incompatibility is evident also in the mechanical properties of the unfilled blend. The modulus and yield strength entered in Table III fall well below corresponding values for the con-
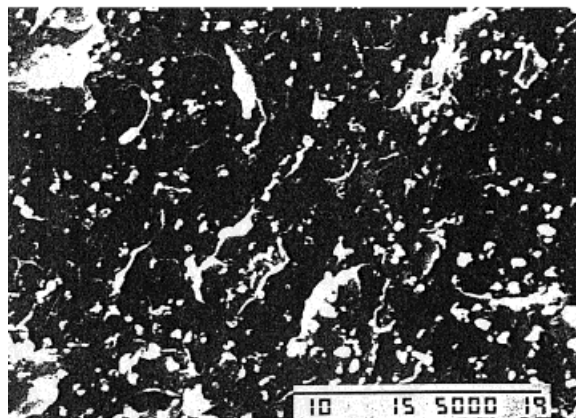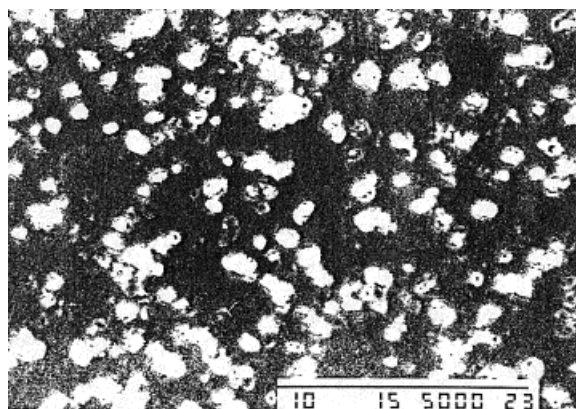

Figure 2 SEM of rutile pigment dispersed by procedure C in PVC matrix. (a) Unmodified rutile. (b) Rutile modified by PS–SiOH copolymer. Pigment concentration is 13 wt %.

Table III   Mechanical Properties of LLDPE/PVC Blends Filled with Surface-Modified Rutile

	Modulus (MPa)			Yield Strength (MPa)		
Filler load (wt %)	0	13	20	0	13	20
	33			6.3		
Rutile, unmod.		49	61		6.9	7.9
R/PS–P4VP		57	62		6.6	5.9
R/PIP/P4VP		72	78		9.0	8.4
R/PS–PAA		52	57		6.2	5.8
R/PS–SiOH		63	76		7.2	7.1

tinuous-phase LLDPE (Table I). The yield point was noted at near 6% elongation, but extension at failure was not sufficiently reproducible to warrant inclusion of ultimate properties. The presence of unmodified rutile has a positive effect on modulus at both loading levels and a slight one at yield, which now occurs at about 15% elongation. As will be evident from IGC data, documented later, the pigment surface has a much higher surface energy than do the polymers. The major LLDPE component may then be expected to adsorb on the available solid surface, accounting for the observation. Pigment coatings raise the modulus of compounds, but the effects are varied. More beneficial effects are produced by the presence of PS–SiOH and PIP–P4VP, these also being the only coatings to generate slight increases in the yield strengths of the compounds. Of the two, R/PIP–P4VP is the better, a fact perhaps attributable to its superior performance with pure LLDPE.

Impact data for the compositions, given as Figure 4, complement the mechanical property results. In this case only compounds containing 13

Figure 3   SE Micrograph of the LLDPE/PVC (75/25) blend.

wt % rutile were examined. A very substantial increase in the impact strength is generated by the PIP–P4VP coating, a lesser one by PS–SiOH. The effects of the other coatings are unremarkable. The results again suggest the existence of different morphology in compounds by using the favorably coated pigment as compared with coatings incapable of producing favorable mechanical property effects. Figure 5 addresses the issue by showing SEM scans of the LLDPE/PVC blend with 13% rutile coated by PS–PAA [Fig. 5(a)], and with the R/PS–SiOH as in Figure 5(b). The magnification in Figure 5(b) is 10-fold greater than in 5(a). The pigment in Figure 5(a) is strongly agglomerated, with particle diameters exceeding 100 μm; there is little if any evidence of bonding with the matrix polymers. Particle sizes in Figure 5(b) are on the order of 10–15 μm; the degree of dispersion is much improved and there is evidence of particle wetting by the matrix phase. Clearly, the degree of interfacial interaction varies substantially in these compounds, mandating further analysis.

Polymer/Pigment Interactions

The IGC techniques noted above were used to obtain quantitative parameters of both acid–base and dispersive interaction at the polymer–pigment interface. The acid–base analysis is limited to contacts between the rutiles and PVC. The polyolefin is a neutral polymer, making an acid–base analysis irrelevant. The route to measuring Ka and Kb, respectively, the acid and base interaction parameters for the stationary phase in IGC, were described elsewhere in detail.[17,18,19] The parameter values are listed in Table IV. Also given is the pair interaction parameter Isp. This combines the Ka and Kb values of contacting materials. In the absence of confirmed theory, the approach used is empirical, the present expres-
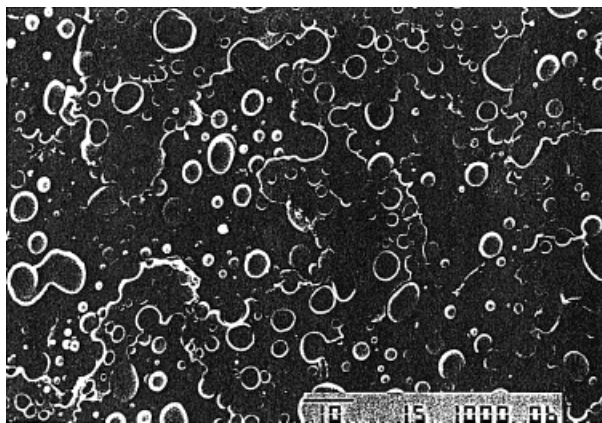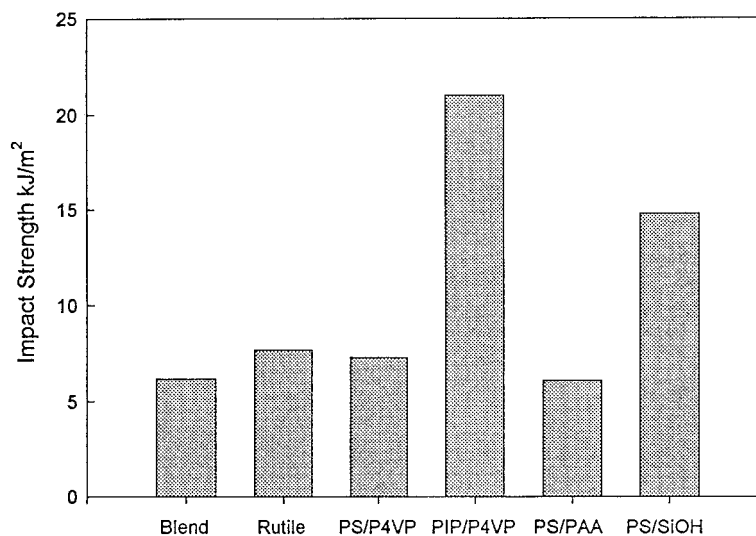
Figure 4 The impact strength of the LLDPE/PVC matrix and three-component blends using the rutile pigments. Mixing procedure C used throughout.

sion justified by the arguments of Kloubek and Schreiber[22]. Thus,

$$\text{Isp} = \text{Ka}_{(R)}\text{Kb}_{(P)} + \text{Kb}_{(R)}\text{Ka}_{(P)} - \text{Ka}_{(R)}\text{Ka}_{(P)}$$
$$- \text{Kb}_{(R)}\text{Kb}_{(P)} \quad (1)$$

where the subscripts R and P represent the rutile and polymer (PVC) components. Account can be taken of dispersive interactions between contacting phases from a work of adhesion parameter Wa^d,

$$\text{Wa}^d = 2(\gamma_R^d \gamma_P^d)^{1/2} \quad (2)$$

Values are reported in Table IV. Both PVC and uncoated rutile are acidic; therefore, interaction between these components is ascribed primarily to dispersion forces. These are substantial, as shown by the high Wa^d value. The presence of the diblocks uniformly lowers the Wa^d, but strongly alters the acid–base interaction balance relative to PVC. PS/PAA further inhibits any contribution to interfacial strength, but the other polymer coatings render the pigment basic, leading to positive values of Isp. On this basis, PS/P4VP and PS/SiOH would be rated as particularly useful modifiers for the PVC–rutile system, a rating confirmed by the mechanical property data reported earlier. The results identify short-range acid–base interactions as an important factor in the morphology of rutile/PVC dispersions and in the solid-state properties of the filled polymer. Strong adsorption of LLDPE on uncoated rutile can also

be inferred from the corresponding Wa^d datum. The presence of copolymers on the pigment surface uniformly lowers the degree of dispersion–force interaction. The slight but positive effects of the copolymers on mechanical properties of filled LLDPE, reported in Table I, are, therefore, more likely due to mechanical interlocking between the tethered polymer and the LLDPE matrix. Judging from the data in Table I, this is most evident with the PIP–P4VP modifier.

The evidence that rutile, modified by PIP–P4VP, is the preferred pigment for the LLDPE/PVC compound appears to rest on that copolymer's ability to behave as both specific interaction and mechanical interlock agent. In this regard, it is effectively a smart polymer,[6,7] its basic P4VP segment bonding with the PVC constituent, and the PIP presumably diffusing into and interlocking with the polyolefin. The PS–SiOH modifier again has the correct acid–base functionality, the basic PS capable of electron exchange with the PVC. The role of SiOH opposite LLDPE is more problematic, the most likely mechanism being enhanced physical adsorption when the modifier is present on the rutile surface. Neither of the remaining block modifiers combines these capabilities. Given the distinct requirements for favorable interfacial conditions between the rutile and the cohabiting polymers, it follows that observed mechanical properties may vary with the detailed method of combining the blend constituents. This is examined in the next section.
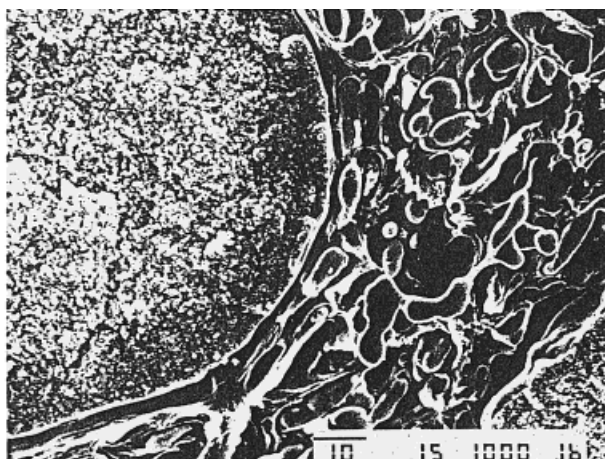
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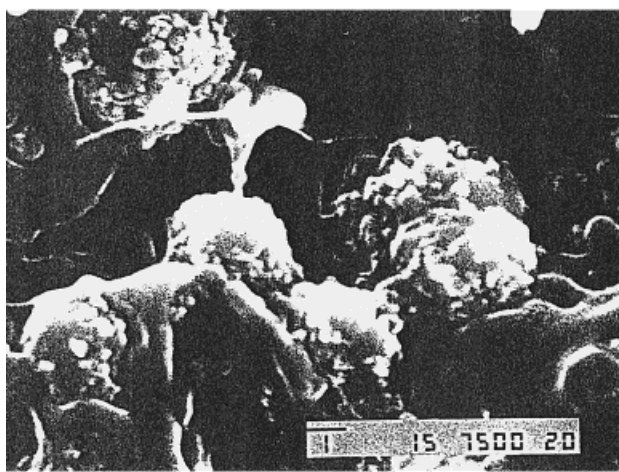
(b)

Figure 5 SEM of the filled LLDPE/PVC blends. (a) Rutile component modified by PS–PAA copolymer. (b) Rutile component modified by PS–SiOH. Pigment concentration is 13 wt %, mixing by procedure C.

Effect of Different Mixing Protocols

Mixing procedures A–D, described earlier, were applied to the LLDPE/PVC blends containing 13 wt % rutile. Following their preparation, the blends were allowed to rest in the environment of the testing device before stress–strain analysis was undertaken. The modulus and yield strength data recorded in Table V are regarded as initial values of the properties. Both modulus and yield strengths appear to be dependent on the mixing protocol. Allowing for a maximum experimental uncertainty of ±5% about the mean values quoted, it is the yield strength that is more sensitive to mixing sequences. The unmodified rutile would be expected strongly to adsorb the LLDPE component, the acidic properties of both rutile and PVC inhibiting adsorption of this pair. Both property parameters attain their highest levels following procedures C and D, which expose the pigment to the premixed polymer pair. These approaches would tend to favor a rapid distribution of the solid between the competing polymer melts.

The modification due to PS–SiOH shows procedure A to generate a compound with lower modulus and a greater tendency to soften at low extension. The properties generated by modes B, C, and D do not appear to vary significantly. An inspection of the Isp data (Table IV) shows the contact between the modified pigment and the PVC component to be characterized by strong acid–base interaction. In procedure A, therefore, access to the rutile surface by the more weakly interacting dominant LLDPE phase would be inhibited, arguably accounting for the observation. The necessary equilibration would take place more rapidly in procedure B, where the pigment surface is first wetted by the LLDPE, and by procedures C and D, where rutile is dispersed in the polymer blend. Modification by PIP–P4VP again strongly favors property development by

Table IV   Surface Energy and Interaction Parameters for Polymers and Rutiles

	γ_s^d (mJ/m^2)	$(Wa^d)_{PVC}$ (mJ/m^2)	$(Wa^d)_{LLDPE}$ (mJ/m^2)	Ka	Kb	Isp[a]
LLDPE	32	—	—	—	—	—
PVC	21	—	—	3.6	2.7	—
Rutile (unmod)	60	71	44	4.8	3.4	−1.3
R/PS–P4VP	27	48	30	2.7	11.6	7.5
R/PIP–P4VP	32	42	32	3.5	6.3	2.5
R/PS–PAA	34	53	33	4.7	2.2	−2.2
R/PS–SiOH	28	49	30	4.0	10.7	6.0

[a] For PVC/rutile pairs.

Table V   Effect of Mixing Procedures on Initial Properties of Filled LLDPE/PVC Blends

Rutile Surface	Modulus (MPa)			Yield Strength (MPa)		
	As is	PS–SiOH	PIP/P4VP	As is	PS–SiOH	PIP–P4VP
Mix. mode						
A	47	55	68	5.2	5.7	7.4
B	48	62	67	5.8	6.7	6.5
C[a]	49	64	72	6.9	7.2	9.0
D	49	62	73	7.0	7.3	8.8

Data refer to blends containing 13 wt % rutile pigment.

[a] Reference mixing mode; see text.

procedures C and D, these producing consistently tougher compositions. In this case, however, it is procedure B that results in the less developed compound. Hypothetically, mechanical interlocking between the rubber moiety now anchored to the rutile and the LLDPE in the first stage of compounding reduces the ability of PVC to compete for surface sites in the subsequent step of this mixing procedure, with negative results on modulus and compound toughness. The evidence of data in Table VI supports the contention that both dispersion and acid–base forces affect the outcome of a specific mixing regime, the role of the acid–base forces being the more evident. The selected mechanical property parameters are not uniquely defined by the blend composition, but appear to depend on the kinetics of component distribution in the course of a selected mixing procedure. Thus, some or perhaps all of the mixing protocols represented here generate nonequilibrium states of component partitioning. The re-

ported properties may be expected to vary with time.

The suggestion of time-dependent variations in the mechanical properties of the ternary LLDPE/PVC blends was examined by using the unmodified rutile as filler. The solids level again was restricted to 13 wt %. Blend samples were aged in a vacuum oven at 100°C, above the glass transition temperature of the PVC constituent. This temperature was selected so as to permit a redistribution of materials within the compound to take place. An approach toward an equilibrium state of distribution was thereby favored. Properties were reexamined after aging, up to a maximum of 30 h. Slight discoloration of compounds after heating for longer times made it impractical to extend the aging experiment beyond this point.

Figures 6 and 7 show the results of the aging experiment. The expected time dependence is documented for both modulus (Fig. 6) and yield strength (Fig. 7). The empirical curve fitting pro-

Table VI   Time-Dependence of Mechanical Properties for LLDPE/PVC Blends Prepared by Various Mixing Modes

Mix. mode	Modulus (MPa)				Yield Strength (MPa)			
	A	B	C	D	A	B	C	D
Aging time (h)								
0	48	47	50	49	5.2	5.8	6.9	7.0
1	50	48	51	51	5.8	6.0	7.1	6.7
2	52	49	51	51	6.6	6.1	7.1	7.0
5	53	50	54	53	7.0	6.2	7.4	7.2
10	55	50	54	55	7.0	6.6	7.7	7.1
24	56	51	54	56	7.4	6.8	7.6	7.3
30	57	52	55	56	7.5	7.0	7.6	7.5

Blends contain 13 wt % unmodified rutile pigment. Aging *in vacuo* at 100 °C.

cedures used here do not identify equilibrium values of the parameters. However, it is apparent that the modulus of the compound tends toward a value near 57 Mpa, and a yield strength in the vicinity of 7.5 MPa. Consistent with the arguments put forth above, mixing mode B in which the rutile is first exposed to the matrix LLDPE, produces a compound furthest removed from the equilibrium state. The absence of acid–base attraction between the unmodified rutile and PVC may be cited as a cause for this, also accounting for the attenuated kinetics of property change toward the equilibrium state. The combination of acid–base and dispersive interactions among the constituents of a polymer system, and the design of mixing procedures used to disperse the constituents represents an important factor in the initial morphology of the compound. This is reflected in turn by the initial mechanical properties and by the magnitude and rate of their response to aging.

CONCLUSION

The following may be concluded from the results of this investigation.

The use of diblock copolymers was effective in modifying the surface properties of a rutile pigment. Depending on the selection of diblock modifier, either acidic or basic interaction properties may be conferred on the pigment surface, as documented by IGC methodology.
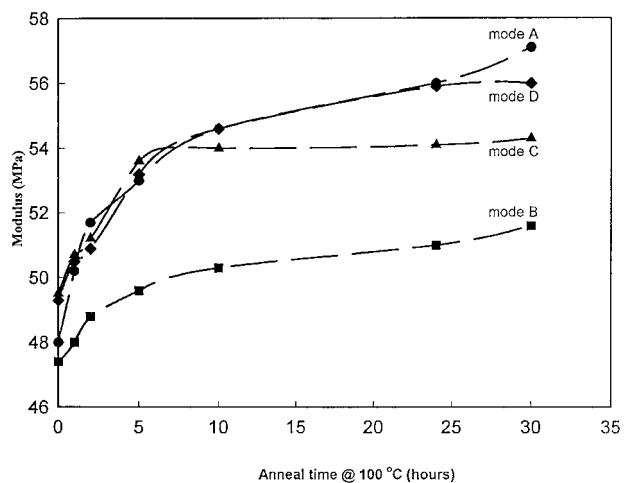

Figure 6 Time-dependent variation of modulus in LLDPE/PVC blends, showing the effect of various mixing modes used to prepare the composition. Unmodified rutile concentration is 13 wt %.
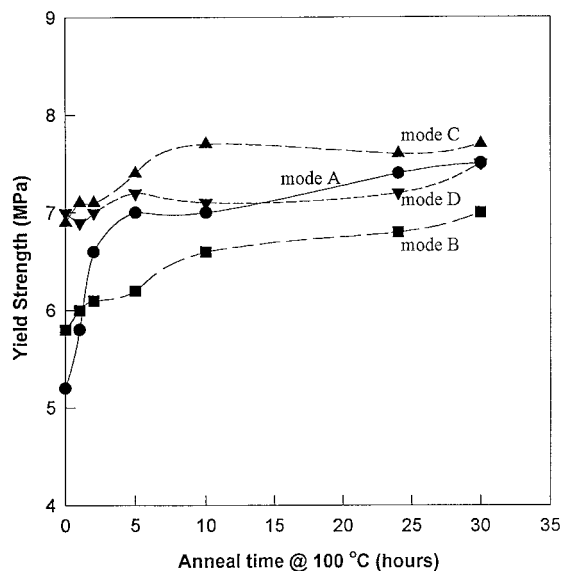

Figure 7 Time-dependent variation in yield strength of LLDPE/PVC blends, showing the effect of various mixing modes used to prepare the composition. Unmodified rutile concentration is 13 wt %.

Modulus, yield strength, and impact properties of binary LLDPE/rutile and PVC/rutile blends were shown to depend on the selection of block copolymer modifier. Optimization of acid–base interaction was beneficial to the dispersion of rutile in PVC and to the mechanical properties of resulting compounds. In the case of LLDPE, morphology and mechanical properties responded primarily to dispersion forces.

The selection of surface modifier was found to affect the properties of ternary LLDPE/PVC/rutile systems. Best results were obtained with the use of modifiers of rutile surfaces such as PIP–P4VP, which combined favorable acid–base interaction between PVC and the 4VP moiety, and a mechanical interlocking between LLDPE and the PIP moiety.

The initial mechanical properties of ternary compounds were found to vary with each of four different mixing procedures. None of the procedures generated equilibrium states of materials distribution (morphology), as shown by the time-dependent change in properties when the compounds were aged at a temperature above the polymer glass transition. The compounds tended to attain a common set of property values as a result of the aging .

The combined effects on initial and time-dependent properties in complex polymer formulations of acid–base, dispersive interactions, and

mixing procedures were found to be important in the blend systems of this investigation. An appreciation of these effects is cited as a desirable element in the design and use of complex polymer systems in general.

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