Surface Modification Strategies for Multicomponent Polymer Systems. V. Interaction States and Mechanical Properties of LLDPE/PVC Blends with Corona-Modified Rutile Pigment

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ABSTRACT: Rutile pigment with preadsorbed monomers of acrylamide (AM) or acrylic acid (AA) has been treated in air corona discharges at various input power levels for times from 30–120 s. Inverse gas chromatographic data showed that the treatments reduced dispersive surface energies and significantly altered the acid/base interaction potential of the surfaces. Inferred is the corona-activated synthesis of oligomeric or polymeric structures anchored to the pigment surface. XPS analyses report modifications in the chemical structure of pigment surfaces, which are consistent with the suggested consequence of corona treatment. When incorporated into LLDPE and PVC host polymers, compounds with the corona-modified rutiles have better mechanical properties than analogues with untreated pigment, notable being improved elastic moduli, yield stresses, and stress/strain relationships at break. AM-modified rutiles were preferable to AA-modified versions in this regard. The addition of treated pigments to immiscible LLDPE/PVC (75/25) blends resulted in similar benefits to mechanical properties, AM pretreatment again being preferred. Stronger acid-base interaction at contacts between corona-modified rutiles and the PVC component is an apparent reason for improved mechanical properties. Speculatively also, AM pretreatments lead to attached chains of sufficient length to entangle with the LLDPE, further strengthening the interphase and relevant bulk properties. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1597–1604, 1998

Key words: rutile; corona treatment; surface energies; acid-base interaction; LLDPE–PVC blends; mechanical properties

INTRODUCTION

The principal theme of this research is to compare various approaches to the modification of surfaces and interfaces in complex systems such as poly-

mer blends with the view of optimizing selected properties of the systems. In the first reports issued from the study[1–4] attention was focussed on the use of diblock copolymers with a variety of functional groups, as modifiers of surfaces and of interfaces in systems based on the immiscible polymer combination of polyvinyl chloride (PVC) and linear, low-density polyethylene (LLDPE). In one part of the work[1,3] the copolymers were applied to rutile pigments in an attempt to modify the solids in a manner appropriate to the interac-

tion characteristics of the component polymers and to evaluate their effectiveness as modifiers of the blends' mechanical properties. Elsewhere[2,4] the emphasis was on the morphology of interfaces in polyblends containing various of the copolymers, and on their effectiveness in modifying the interfacial tension of the PVC/LLDPE pair. Considerable emphasis has been and continues to be placed on quantitative measurements of specific (or acid-base) interactions as a means of rationalizing observations and of providing guidelines for the preferred modification strategy to be followed to targeted performance ends.

An alternative to the use of synthetic polymer additives is to modify the surfaces of system components by electrical discharge methods. Among these corona and cold-plasma discharges are leading candidates. Cold-plasma discharges are powerful proven methods to generate wide-ranging modifications to component surfaces,[5] but their general use is somewhat hampered by the complexity of reactions and by the cost of suitable equipment. In contrast, corona-discharge technology has a long track record of use in the polymer industry, notwithstanding the admittedly complex physics and chemistry that corona treatments initiate at solid surfaces.[6–8] The range of surface modifications accessible to coronas also is formidable. Surface oxidation and crosslinking reactions are usually the results attributed to corona treatments of polymer surfaces; graft polymerization on polymer surfaces sensitized by corona discharges[9] adds to the range of effects that may be expected.

In the present work, corona discharges have been applied to the surfaces of rutile pigments, which had been saturated with monomers of acrylic acid (AA) or acrylamide (AM). The objective was to show whether or not corona treatments under various controlled conditions could initiate polymerization at the pigment surface. The corona-treated solids were then used as fillers in PVC, LLDPE, and in blends of these polymers. We report on interaction states and mechanical properties in these blends.

EXPERIMENTAL

Materials

The rutile used in this work was supplied as a dry powder by Tioxide North America Inc. No surface coating was applied by the manufacturer, nor at this site. Standard nitrogen adsorption (B.E.T.) analysis showed the rutile to have a surface area of 10.0 m^2/g, corresponding to a mean particle size of 22 μm. The LLDPE, a melt flow index 1.0 polymer with M_n = 33,000 g/mol and M_w = 115,000 g/mol was obtained from Union Carbide Corp. Synergistic Chemicals Inc. was the supplier of a commercially produced PVC. The resin had a M_w = 54,000 g/mol and contained 7 phr Advastab TM-821 SP thermal stabilizer.

The following thermomechanical treatments were applied to single and blend polymers. Compounding was done in a Brabender Plasticorder at 175°C. To prepare rutile-filled specimens of LLDPE and PVC, the host polymers were melted (LLDPE) or gelled (PVC), whereupon pigment was added and dispersed for 5 min at a rotor blade speed of 50 rpm. This was sufficient to attain steady-state torque readings in all cases. The study of blends was restricted to the weight ratio of LLDPE/PVC = 75/25. Blend preparation called for first melting the LLDPE host, then adding the PVC and mixing for 5 min. Thereupon the rutile was added, and blending continued for an additional 5 min. Samples suitable for mechanical property evaluation were prepared by compression molding at 180°C, and cooling in the press under pressure.

Corona Treatment

A laboratory scale apparatus, described previously,[10] was used to modify the surface properties of rutile. The apparatus consists of two flat aluminum electrodes and a quartz plate as a dielectric spacer. Teflon rings placed on the bottom electrode form a cylindrical cell, capable of housing powder samples. In this work, 2-g samples of rutile were processed per run. The corona equipment was operated at 20 mA, a frequency of 3.5 kHz, and with a voltage drop of 15 kV. During corona treatments the temperature was controlled at 24°C and the relative humidity at 50%. The combination of treatment power and times applied to rutile samples is listed in Table I. Rutile specimens to be treated were first saturated with AA or AM monomers. In the case of AM, the powder was immersed in 5 wt % solutions of AM in tetrahydrofuran. The suspensions were stirred and evaporated to dryness in Rotovap apparatus. Additional drying under vacuum ensured total removal of the solvent. AA was deposited onto rutile under vacuum in a glass vessel maintained at 120°C. Following drying, rutile samples overcoated by AA or AM were hand ground to particles in the range 250–400 μm, for use in IGC experiments.

Table I   Time and Voltage for Corona Treatment

Sample	Time (s)	Voltage (kV)
Corona-control	120	10
AM-1	30	4.5
AM-2	30	10
AM-3	120	4.5
AM-4	120	10
AA-1	30	4.5
AA-2	30	10
AA-3	120	4.5
AA-4	120	10

Surface Analysis

The surfaces of rutile samples before and after corona exposure were analysed by XPS, using the VG Escalab MK II system with unmonochromated Mg Ka radiation (1253, 6 eV). Operation was at 12 kV and 20 mA, at a pressure of $\sim 10^{-8}$ Torr. Under these conditions resolution of the C1s peak was about 0.8 eV. The apparatus was calibrated and periodically rechecked with Cu, Ag, and Au spectral lines.

IGC Measurements

The experimental protocols for IGC measurements were those fully described in recent literature.[11–14] They were applied to evaluate the effects of corona treatment on the acid-base interaction characteristics of pure rutiles as well as of those previously saturated with AA or AM monomers. Briefly, rutile samples were packed in previously washed, degreased, and dried stainless steel columns 1.5 mm in diameter and 15 cm long. These were placed in a Varian 3400 gas chromatograph equipped with thermal conductivity and flame ionization detectors. Columns were conditioned at 120°C for at least 4 h, under a flow of dry helium, which also served as the carrier gas for IGC determinations. These were conducted in the range of 30–80°C.

Stationary phases were probed by nonpolar and polar vapors injected at infinite dilution. The nonpolar probes were the n-alkanes from C6–C9, which reported on the dispersion-force interaction between stationary and vapor phases. This followed from the well-established expression[15]

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

where the γ^d are the dispersive surface energies of the solid, s, and of the vapor in the liquid state, l, N is Avogadro's number, a is the molecular area of the adsorbed probe molecule and c is a constant defined by the selection of a standard state. In this work, the a values used were those reported in ref. 15. Equation (1) calls for the generation of a straight line when the left hand side is plotted vs. $a(\gamma_l^d)^{1/2}$ for the alkane probes. The slope of the line defines the surface energy parameter of the solid phase and serves as a reference line for the evaluation of acid-base interactions.

The acid-base (specific) interaction potential of rutiles was assessed by measuring their retention characteristics for polar probes, selected on the basis of their electron donor and acceptor numbers, DN and AN, as given by Gutmann.[16] They included the acids chloroform and dichloromethane, the bases diethyl ether and tetrahydrofuran, and the amphipatic vapors of acetone and ethyl acetate. Retention times for these probes deviate from the reference line of eq. (1) when the stationary phase is able to act as electron acceptor and/or donor. The normal distance of the experimental datum from that line is expressed by

$$\Delta G_{ab} = RT \ln Vn/Vn^{\text{ref}} \qquad (2)$$

Here, ΔG_{ab} is the acid/base contribution to the free energy of desorption of the polar probes. The acid and base interaction constants of the stationary phase, Ka and Kb require the determination of the enthalpy term, ΔH_{ab}, which is obtained from the temperature variation of the free energy term. Thus,

$$\Delta H_{ab} = KaDN + KbAN^* \qquad (3)$$

where AN^* and DN are the acceptor and donor numbers of the vapor probes, as given by Gutmann.[16] The acceptor number has been modified by the corrections suggested by Riddle and Fowkes.[17]

In all IGC experimentation, retention times for each probe were averaged from at least triplicate injections, with standard deviations not exceeding 3%.

Mechanical Properties

An Instron table model tester was used to evaluate mechanical property indicators. Specimens were cut from compression molded sheets, according to the prescription of ASTM-D-638M. Tests

T=50 °C

Figure 1 Application of eq. (1) to corona-treated rutile. T = 50°C.

were conducted at a crosshead speed of 20 mm/min. Each result reported is the average of at least five tests, with a standard deviation not exceeding 8%.

RESULTS AND DISCUSSION

Rutile Interaction Characteristics; IGC Data

Retention data for each of the rutile samples were well represented by eq. (1), as shown in Figure 1

for the rutile sample pretreated with AM monomer, then corona treated at 10 KV, 30 s. The figure also shows that the solid acted as both electron acceptor and donor, with all of the polar probes falling well off the reference line defined by n-alkane vapors. A summary of γ_s^d, Ka, and Kb values is given in Table II. The high dispersive surface energy of control (uncoated, untreated) rutile is at a level expected from earlier IGC investigations on metal oxide powders. Corona treatment (identified as corona-control, Table II) increases the surface energy datum by about 10%, indicating augmented polarity, perhaps due to surface reactions leading to a greater concentration of oxygen. The γ_s^d of presaturated, corona-treated pigments is substantially reduced, and the reduction is systematically more pronounced as the intensity and duration of corona treatment increases. The values in the range of 25 mJ/m^2 are very similar to those of polymers.[18] One may infer, therefore, that the corona treatments have been successful in generating strongly anchored moieties, perhaps in the form of grafted oligomeric or polymeric chains, which have shielded much of the original pigment surface.

The K parameters are equally interesting. Corona treatment of the control rutile increases both Ka and Kb. The solid remains predominantly acidic ($Ka/Kb > 1$), but the total interaction potential, given by ($Ka + Kb$), rises by more than 20%. Again, increased surface polarity is indicated. Each of the corona treated solids with preadsorbed monomers shifts to amphoteric or predominantly basic interaction. This is understandable for AM modifications, but somewhat surprising in the AA-modified cases. Earlier,[1] we reported that the adsorption of PS/AA diblocks generates rutiles with Ka/Kb

Table II   Surface Characteristics for Rutile-Treated and Untreated at 70°C

Sample	γ_S^D (mJ/m^2)	K_a	K_b	K_a/K_b	$K_a + K_b$
Control	52.1	0.52	0.28	1.86	0.80
Corona-control	57.2	0.65	0.39	1.67	1.04
AM-1	42.1	0.48	0.67	0.72	1.15
AM-2	32.1	0.23	0.82	0.28	1.05
AM-3	30.4	0.17	0.99	0.17	1.16
AM-4	22.2	0.22	0.98	0.23	1.20
AA-1	45.1	0.29	0.30	0.96	0.59
AA-2	26.0	0.27	0.35	0.77	0.62
AA-3	22.3	0.17	0.36	0.49	0.44
AA-4	16.6	0.18	0.24	0.75	0.42

Table III   Surface Composition of Various Samples

Sample	$T_i\%$	C%	O%	N%
Control	21.2	23.3	55.0	0
Corona				
control	17.9	30.0	52.1	0
AM-1	11.6	37.1	45.8	5.4
AM-4	11.0	36.1	47.1	5.6
AA-1	12.7	37.4	49.9	0
AA-4	11.4	37.3	51.3	0

$\sim$ 2; a speculative but reasonable explanation for the present result may be the dehydration of the AA monomer by the rutile, forming the basic anhydride, which is then chain extended by the corona discharge to form a predominantly basic macromolecule. The total interaction potential of rutiles modified by the AM route is clearly greater than that of corresponding solids using the AA monomer. Indeed, the presence of AM structures elevates the surface interaction potential above those of bare and air corona-modified versions of the pigment. The total interaction potential of AA-modified solids falls below that of the control rutiles, indicating this modification to be less likely to form specific, short-

range interactions with contacting polymers. XPS data are called for to elaborate on the suggestions drawn from the IGC analyses.

XPS Analysis

XPS experiments were restricted to the unmodified control and the corona-treated control rutiles, and to samples AM-1, AM-4 and AA-1, AA-4, these representing the extremes of corona exposures of the AM- and AA-doped materials. The results of analyses are given in Tables III and IV. In the former are listed surface concentrations of C, O, N, and Ti. These are normalized so that the sum equals 100 atom %. Trace concentrations of K, Na, and S were found on the samples but are not tabulated. More detailed analysis, in the form of the components of high resolution C1s, O1s, and N1s envelopes, is given in Table IV. A striking feature in Table III is the rather large quantity of C in the control and the uncoated, corona-treated rutile. The impurity responsible for this has not been identified. The expectation of increased oxygen present in the corona-treated control solid is not met; however, this is probably due to sample preparation for XPS analysis, which required comminuting the corona-treated specimen. The break-up of rutile clusters resulting from this step would introduce substantial

Table IV   Components of C_{1s}, O_{1s}, and N_{1s} Photopeaks

Binding Energy (eV)	Species	Untreated	AM-1	AM-4	AA-1	AA-4	Uncoated
C_{1s}				Percent of C_{1s} Photopeak			
282.93	Ti—C	7.4	4.0	2.4	5.4	4.36	2.7
285.0	C—C	75.5	26.0	40.2	14.6	29.6	78.4
285.9	C—NO$_2$, C—C=O	—	36.0	25.7	58.8	40.0	
286.5	C—O	10.5	—	—	11.8?	8.3	8.7
287.4	N—C—O	—	16.2	14.4	—	—	—
288.8	OC=O	6.6	17.8	17.3	10.0	17.7	5.6
O_{1s}				Percent of O_{1s} Photopeak			
530.0	TiO$_2$	81.7	60.7	60.3	69.1	56.0	77.8
531.7	N—C=O, C=O	15.1	22.7	25.1	20.5	32.8	17.2
533.0	C—O	3.2	16.6	14.7	10.4	11.2	5.1
N_{1s}				Percent of N_{1s} Photopeak			
399.8	C—N	—	50.0	51.4	—	—	—
400.8	N—C=O	—	50.0	48.6	—	—	—

Table V   Tensile Properties of LLDPE and PVC Compounds

LLDPE	Modulus (MPa)	Yield Strength (MPa)	Tensile Strength at 500% Elongation (MPa)
PE-control	250	7.5	7.4
R/corona-control	375	9.8	10.0
R/control	310	8.9	8.7
R/AM-4	380	10.5	11.6
R/AA-4	390	9.8	10.1

PVC	Modulus (MPa)	Yield Strength (MPa)	Tensile Strength at Break (MPa)	Elongation at Break (%)
PVC-control	2600	57.5	256	25.4
R/corona-control	2900	58.0	250	19.7
R/control	2900	58.0	260	20.3
R/AM-4	3320	64.0	270	23.2
R/AA-4	3090	58.4	265	21.5

amounts of "new," untreated surface, thereby affecting the oxygen reading. In spite of this complication, the corona-treated rutile has a significantly reduced Ti and an increased C content, showing the ability of the corona in modifying the surface composition. More significant compositional changes are evident in corona-treated samples with preadsorbed monomers. The AM-containing samples report appreciable N content, while in AA-doped rutiles there are further readjustments in the balance of Ti, O, and C concentrations. Somewhat surprisingly, the differences between AM-1, AM-4 and between AA-1 and AA-4 are small, the most notable effect being a somewhat greater oxygen concentration in the more intensively corona-treated specimens. The persistence of Ti peaks in all AM and AA-doped specimens again may be attributed to the generation of untreated surfaces by the forementioned grinding operation. An alternative is incomplete coverage of the available rutile surface by the corona-initiated chain-extension reactions.

Analysis of the photopeak components in Table IV indicates the presence, in significant amounts, of NC=O structures in samples AM-1 and AM-4 and of OC=O groups in AA-1 and AA-4. Clearly, chemically distinct chains have been anchored in the rutile surface by these preadsorption corona procedures. Their impact on interaction properties is considerable, as already discussed. Their influence on mechanical properties is the subject of the next section.

Mechanical Properties

The property parameters for rutile-containing LLDPE and PVC blends are given in Table V. Reported are moduli and yield strengths of systems containing 15 phr of rutile pigment. In addition, the tensile strength of filled LLDPE at 500% elongation is tabled, and in the case of PVC systems, the table contains tensile strengths and elongations at break. Untreated and corona-treated control fillers were used as were rutiles with preadsorbed AM and AA, treated under the most intensive corona condition, labeled R/AM-4 and R/AA-4. The performance parameters for LLDPE and PVC compounds containing these pigments are listed in Table V. Although the effects of corona treatment and of surface modification by AM and AA structures is relatively slight, the mechanical responses are significant and follow a distinct pattern. The moduli and yield strengths of LLDPE compounds respond to the presence of rutile. Corona treatment further augments the polymer modulus by some 20%, but there is little distinction between corona treatments on bare and previously doped versions of the pigment. The yield strength and the strength at 500% elongation also respond positively. Here, the incorporation of R/AM-4 is particularly beneficial, suggesting that this state of modification leads to better particle dispersion and stronger interaction at the LLDPE-filler interface. Such an interaction cannot be attributed to acid-base effects, the LLDPE being incapable of functioning

Table VI   Tensile Properties of PE/PVC Compounds

Compound	Modulus (MPa)	Yield Strength (MPa)	Tensile Strength at 500% Elongation (MPa)
PE/PVC-control	390	7.6	8.0
R/control	500	7.4	8.1
R/corona-control	510	8.8	8.6
R/AM-4	565	9.2	10.0
R/AA-4	530	8.2	8.5

as acid or base. An alternative origin must be sought. One possibility is that unlike AA modification, AM modification produces anchored chains of sufficient length to entangle with the host polymer, forming stronger network structures in the interfacial region. A change in the crystalline–amorphous ratio in the LLDPE is also a possible contributing effect, and one open to questioning by DSC experimentation, now planned. The pattern in PVC compounds is generally similar: untreated rutile increases the system's modulus but does not alter the yield strength. Here, there is no discernible advantage for the use of corona-treated bare rutile. Significant response is observed in compounds using R/AA-4 and R/AM-4, the latter again generating the largest increments in yield strength and in the ultimate performance parameters. In this case, favorable interactions between the acidic PVC matrix (Ka = 0.36, Kb = 0.26, ref. 18) and the strongly basic version of the pigment (see Ka and Kb values, Table II) may account for the observations.

Table VI presents the mechanical property data for LLDPE/PVC (75/25), again containing 15 phr rutile. The effects of corona treatments broadly follow the trends seen in LLDPE compounds. The introduction of rutile enhances modulus, leaving the yield point and the tensile at high extension and tensiles at 500% elongation unchanged. Following corona treatment the tensiles at moderate and high extension increase, with maximum effects again associated with the use of R/AM-4. Clearly, the use of corona-treated pigments, notably those modified by the presence of moieties based on AM monomer, is beneficial for the enhancement of properties in complex LLDPE–PVC blends.

To date, the study has not quantitatively described the graft structures generated by the combined monomer sorption–corona treatment operations. The persistence of effects attributable to the pigment surface modifications following extended shearing and heating (as in the preparation of specimens for mechanical property testing) shows, however, that these structures are strongly anchored to the pigment surface. Further, the corona treatments applied here have not necessarily produced the optimum surface modification, and thus the maximum changes in mechanical properties of systems containing these solids. A broader development of the approach, including the corona modification of a wider range of inorganic and organic pigments and fillers, is clearly indicated.

CONCLUSION

The following may be concluded: (1) Corona treatment of rutile pigment with preadsorbed acrylic acid or acrylamide monomer has resulted in the significant surface modification of the solid. (2) Corona treatments affect the surface energy of rutile and the acid–base interaction potential of the pigment. The effects become increasingly evident as the intensity and duration of corona treatment increases. (3) Although the detailed structures produced by coronas in AA and AM-doped rutiles have not been identified, these are sufficiently strongly anchored on the rutile to withstand the shear and thermal histories associated with the preparation of blends and of specimens suited for mechanical property evaluation. (4) AM-modification is the more effective in improving the moduli, tensile, and elongation characteristics of PVC and LLDPE hosts. In the case of PVC, the benefits may originate in stronger acid–base interactions. In LLDPE compounds, the superiority of AM-modification may lie in the generation of anchored moieties sufficiently long to chain entangle with the host polymer. (5) Doped, corona-treated rutiles produce analogous improvements in the mechanical properties of im-

miscible LLDPE/PVC (75/25) compounds. The strategy of corona treating previously doped surfaces of rutile and other pigments or fillers shows sufficient promise to warrant broader exploration.

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