

Compatibility Study of Waste Poly(ethylene terephthalate) with Poly(vinyl chloride). II

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ABSTRACT: In this study, exploration of possibilities for use of recycled poly(ethylene terephthalate) (PET) in powder form as a filler in the PVC matrix was made. Powdered PET surfaces were modified by plasma to enhance the degree of interaction and, hence, the compatibilities. For modification, a series of different chlorine-containing monomers at two plasma operational conditions selected were used, in addition to the direct use of an oligomer of vinyl chloride. A series of mechanical, thermal, and surface energy analyses made with the composite samples prepared showed that it is possible to improve the properties by employing proper surface modification, which, in some cases, can even lead to synergistic results. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 765–774, 1998

Key words: plasma; surface modification; PET/PVC blends

INTRODUCTION

Plastic packaging materials that form the major part of the plastic waste stream (mainly due to their short lifetimes in use) draw much criticism in the environment and they are required to be disposed of and/or recycled properly. The necessity of recycling certainly is not only for ecological but also for economical reasons.¹ Already, there have been a number of different possibilities found and methods established for the recycling of polymers,^{2,3} including exploration of the possibilities of using recycled poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC) together.⁴ The PET and PVC case has drawn considerable interest in this context because these are two of the most widely used packaging materials and, so far, there is no method established for their reutilization, which certainly is challenging.

PET and PVC are mutually immiscible, which allows a successful PVC–PET composite system

to be produced. In addition, the high melting point of PET (about 300°C) leads to a high degree of thermal degradation and dehydrochlorination of PVC, which critically begins at 130°C, making the classical melt-blending technique impossible to apply.

In this series of studies, exploration of the possibilities for the use of recycled PET in powder form as a filler in the PVC matrix is being made. To enhance the degree of interaction and compatibilities, the surfaces of powdered PET are modified, for which vinyl chloride and a series of chlorine-containing monomers at certain plasma conditions are used separately. In addition to the preparation and use of plasma surface-modified fillers, an oligomer of vinyl chloride is also used directly in the composite sample preparation. The effects of surface modification of a filler and use of an oligomer on various properties of the composites were determined separately by mechanical, thermal, and surface energy analysis methods.

EXPERIMENTAL

The PET used in this study is a soft drink bottle grade product of SASA A.Ş. (Adana), while PVC

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Table I Properties of PET Used

Property	Value	Unit
T_g	74.5	°C
T_m	340	°C
Solubility parameter (δ)	21.9	$10^{-3} (\text{J}/\text{m}^3)^{1/2}$
Intrinsic viscosity (η)	0.844	dL/g
Size	74	μ

is produced by Petkim A.Ş. (Petrochemical Ind. Inc.) with the trade name PETVINIL Code S.23/59; both are products of Turkey. Some characteristics of the PET and PVC used are presented in Tables I and II.

The chemicals used in the plasma [carbon tetrachloride (CCl_4), 1,1,2,2-tetrachloroethane (TCE), 1,1-dichloroethylene (DCE), and vinyl chloride monomer (VCM)] were all reagent grade and were used without further purification (Table III). The low molecular weight vinyl chloride copolymer (VCO) used was a side product of the VCM unit of Petkim containing 30% chlorine and it was used with compositions of 0.5–1 and 5% in blends without application of the plasma.

PET granules were powderized at room temperature using a mechanical grinder and sizes up to 74 μ were separated and used. The surface of the PET powders were modified at various plasma conditions selected where there are only plasma-treatment effects, but where no appreciable plasma polymerization is expected.^{5,6} The details of the plasma system used was presented before.⁴ The monomers are used under two different plasma conditions, which are termed “low” and “high,” where, basically, the plasma powder and monomer flow rates applied are different and the plasma durations for both are kept at 25 min (Table IV).

After treatment of the PET powder surfaces in the plasma, they are filled into the PVC matrix at 25 and 50% compositions—both selected as the

two extreme and most unfavorable cases—and samples are prepared by mixing in a Brabender Plasticorder Model PLV 151, without application of any heat. Then, the mixture is pressed in a PHI platen press at 190°C under a load of 30,000 lbs between steel molds from which test samples are cut. The samples prepared sat for 24 h to avoid any effect of the thermal history. One should note that the preparation of the composites with a loading of 75% PET were not too successful due to the production of highly friable and heterogeneous systems.

The results of the surface characterization of powders and film samples by ESCA will be presented separately in another communication in preparation. Static mechanical tests are done using an Instron TM 1102. The sample gauge lengths are kept at 3.5 cm with an average width and thickness of the samples of about 0.3 cm and 120 μ , respectively. All tests are done with the same crosshead speed of 5 cm/min. For DSC tests, a TA Instruments 910S Model thermal analyzer is used. As PVC is heat degradable, heating is applied until 120°C for samples that contain PVC.

Contact angle measurements are made to check the existence of any correlation between surface energies and static mechanical test results and an electronic microbalance (Sartorius M25D) equipped with a motor bike (vertical mobile stage, Oriel Model 18008) is also used. The sample sizes tested were typically $5 \times 5 \times 0.2$ mm and the linear speed of the vertical stage is kept constant at 1 m/s. During the experiments, diodomethane is used as the probe liquid for Lifshitz–van der Waals interactions while ethylene glycol and formamide are used for acid–base interactions. In addition, *n*-decane is used as a completely wetting liquid to determine the perimeters of the specimens. All liquids mentioned were of analytical grade and were used at 20°C as supplied. The microbalance system and related procedure are described in another communication.⁵

Table II Properties of PVC (Petvinil, S-23/59) Used

Property	Value	Unit
T_g	81	°C
Softening temperature	130	°C
Solubility parameter (δ)	19.2	$(\text{J}/\text{m}^3)^{1/2}$
Intrinsic viscosity (η)	0.525	dL/g
Size	>600	0.177–0.0088 mm
Apparent packing density	0.58–0.68	Sieve g/kg (psat) kg/dm^3

Table III List of the Monomers Used in the Plasma Reactor

Monomer	Boiling Point (°C)
Carbon tetrachloride	76.8
1,1,2,2-tetrachloroethane	146
1,1-dichloroethylene	47
Vinyl chloride	-24

SEM analyses are applied in a JSM 6400 Noran system. Samples are coated with a Pa–Au alloy. Magnifications used are between 140–370.

Viscosity measurements are done, first to compare some of the results obtained in this study with that of the first part⁴ and, second, to shed some more light on the studies of the interrelation of the degree of polymer compatibilities in bulk with that of solution viscosities,⁶ at least, qualitatively. For this, an Ubbelohde-type viscometer and a mixed solvent system (phenoltetrachloroethane, with the ratio of 1 : 3 w/w) is used, at 25°C, the results of which are expected to reflect the relative trend. It should be noted that there was neither any precipitation nor gel formation observed in the polymer solutions employed.

Table IV Plasma Conditions

Measure	Low Plasma Condition	High Plasma Condition
Output (watt)	10 W	17 W
Pressure (Mbar)	4.5×10^{-1}	5.1×10^{-1}
Flow rate of monomer (mL/min)	60	120

RESULTS AND DISCUSSION

Mechanical tests are followed mainly by ultimate tensile strength and strains as well as by Young's moduli values for the blends prepared with virgin and/or modified components. Results of both ultimate strength (UTS) and strain (UTE) values have shown that (Fig. 1 for UTS at a low plasma condition; the results were similar for UTE, which are not presented) the modification of the PET powder surfaces in the plasma tested did not result in any dramatic change in the ultimate values, although for DCE- and TCE-modified samples, slightly improved results were obtained. UTE results for DCE at both high and low plasma is presented

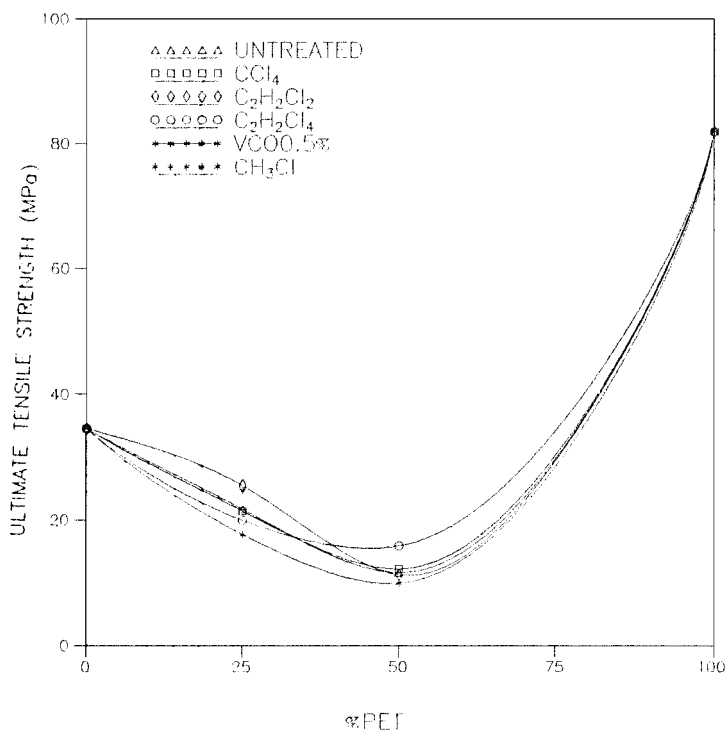


Figure 1 UTS versus percent composition for the composites with untreated and treated PET under low-plasma conditions.

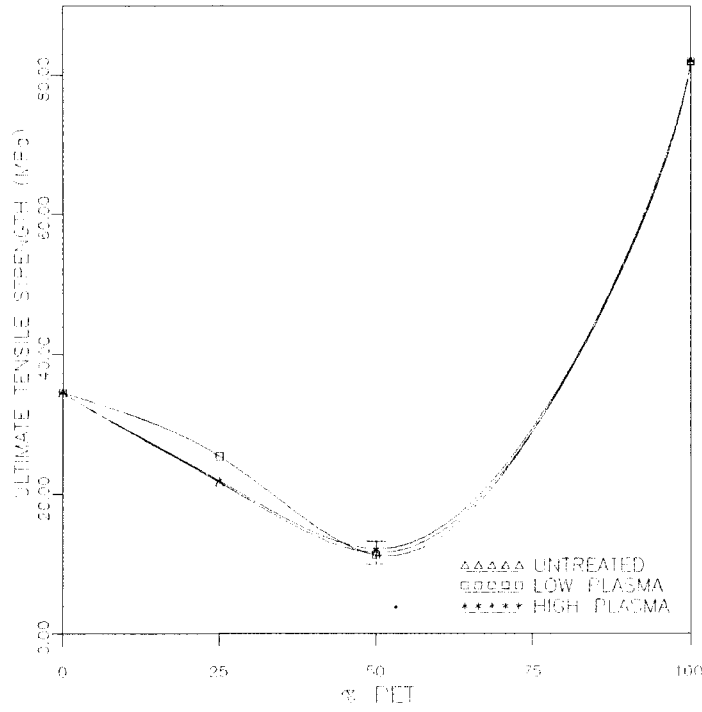


Figure 2 UTS versus percent composition for the composites with untreated and DCE treated PET under high- and low-plasma conditions.

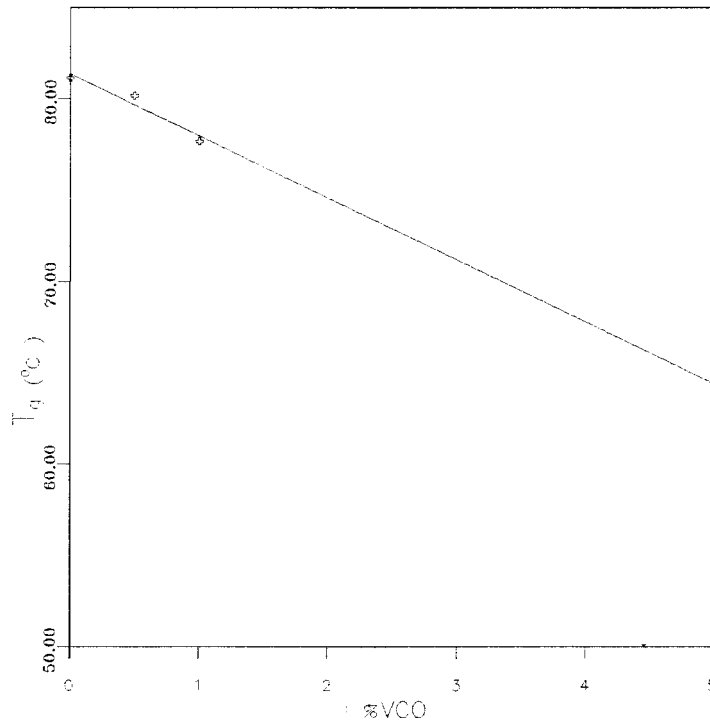


Figure 3 Change in T_g values, abstracted from DSC thermograms observed with varying VCO contents (wt/wt) in blends.

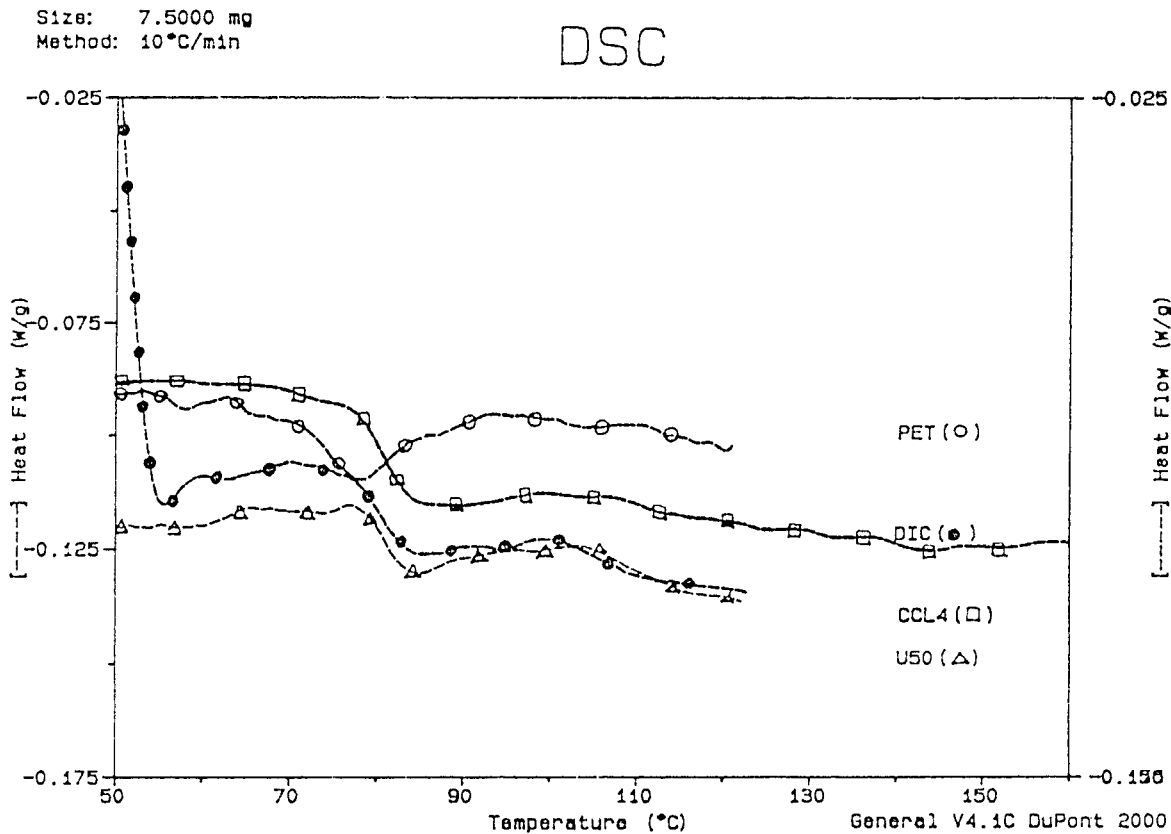


Figure 4 DSC thermograms for PET and PET/PVC blends prepared with untreated and untreated PET at 50% loading for the latter. Letters show plasma media.

in Figure 2. At this point, one should consider, on purpose, the most unfavorable conditions selected, which are that (1) the filler particles used have quite large sizes (74 microns), (2) the compositions prepared are unusually high (with 25 and 50% filler), and (3) the negligibly small amount of modified layers expected at the filler surfaces after plasma modifications, due to the plasma conditions selected.

As for the VCO-added cases, for the samples with 0.5, 1, and 5% VCO and 25% PET loadings, it is realized that both UTS and UTE values are decreased by increasing the VCO contents, most probably showing its plastifying effect on the PVC matrix, as expected. This is also proved by the DSC results (Fig. 3). As seen from other DSC traces, there is no such plasticization effect of the plasma products observed for the plasma-modified samples (Fig. 4).

Although the conditions selected are unfavorable, still some interesting results are obtainable from other mechanical tests: blends prepared with DCE and TCE plasma-modified PET are

found to have much higher Young's moduli values than those of their untreated counterparts and other modified samples (Fig. 5). The composites prepared with TCE plasma-modified PET even have synergistically higher moduli values than expected, while the composite samples with DCE plasma-modified PET have values very close to the additivity line, showing an improved degree of compatibilities gained by this modification. The results presented in the figure are for the high plasma condition, which was shown to be less effective than the low one (Fig. 2). The result obtained for the low plasma was more dramatic, which is not presented here.

In the previous study,⁴ the degree of compatibility in the solid state was attempted to be extrapolated from that of the dilute solution behavior using the Krigbaum-Wall method.⁶ This method is known to be based on the intrinsic viscosity values as well as on the parameter of (Δb) and it uses a viscometric technique. In that study, it was concluded that VCM plasma modification of PET powder surfaces increased the interaction—

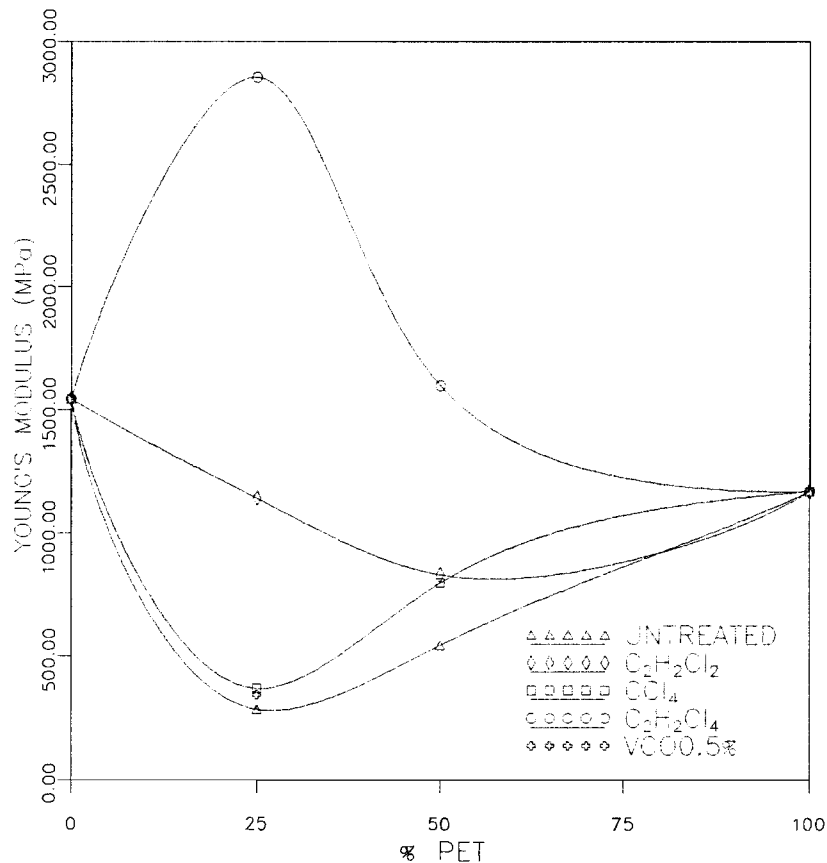


Figure 5 Young's modulus versus PET compositions for PET/PVC composites with PET treated under high-plasma conditions as well as with VCO-added samples.

hence, its compatibility with PVC. To have comparable results, the same method was applied to all samples involved in this part for all composite samples both with modified and unmodified PET and the relative changes observed in the viscosities were noted.

Figure 6 presents the intrinsic viscosities of samples with high-plasma-treated and untreated PET. If one considers the additivity line corresponding to the complete compatibility case, then the ones with a smaller or larger deviation from it would correspond to the cases where there is a larger or smaller degree of compatibility, respectively. From the figure, it is seen that the VC or TCE plasma treatment of PET led to the smallest deviation from this line, while samples prepared with DCE plasma treatment are rather marginal. As mentioned above, for the moduli and ultimate strength values of the same samples, the largest deviations from the additivity line were observed. Certainly, after the viscosity studies, one can conclude that VC plasma treatment of PET should

yield a more compatible system if the treatment of the method itself and the concept of extrapolation of the solution behavior to the bulk are applicable.⁴ Since both the viscosity and static mechanical test results contradict each other for some cases, at this stage, we can point out the fact that, qualitatively, the extrapolation approach may not be completely correct.

To shed some more light on the studies in progress of another work, where the interrelation between surface energies and bulk properties is of interest, the surface energies of all composite samples prepared were obtained. Figure 7 presents the surface energies of composites prepared with untreated and DCE high- and low-plasma-treated PET. As seen from the figure, the surface modification of one of the components (PET) allows the surface energies of the composite to increase and approach the linear line, which is better for the low plasma treatment case. Although any solid conclusion cannot be made at this stage for the results obtained, it is to be noted

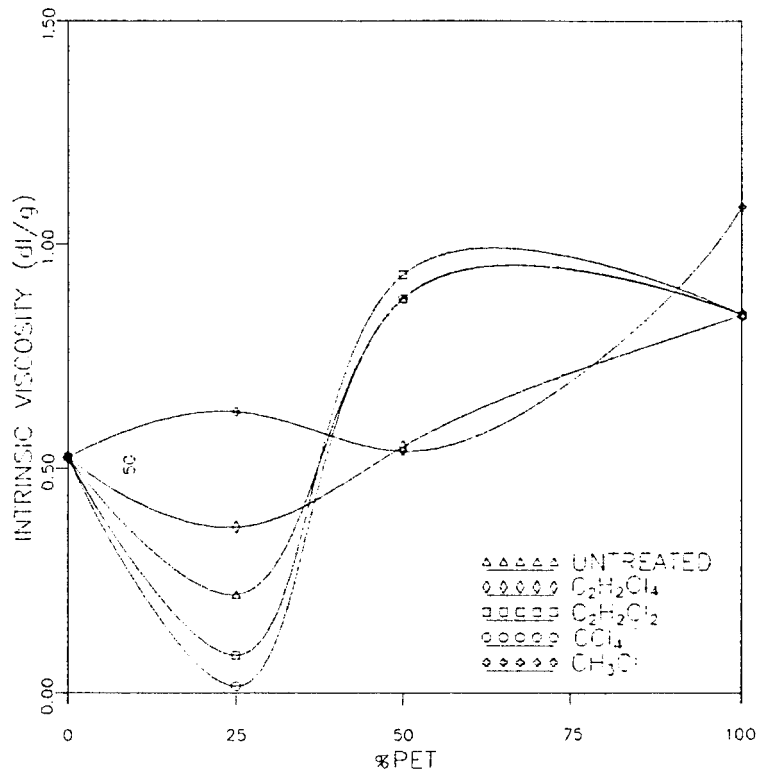


Figure 6 Intrinsic viscosities of samples prepared with untreated and plasma-treated PET.

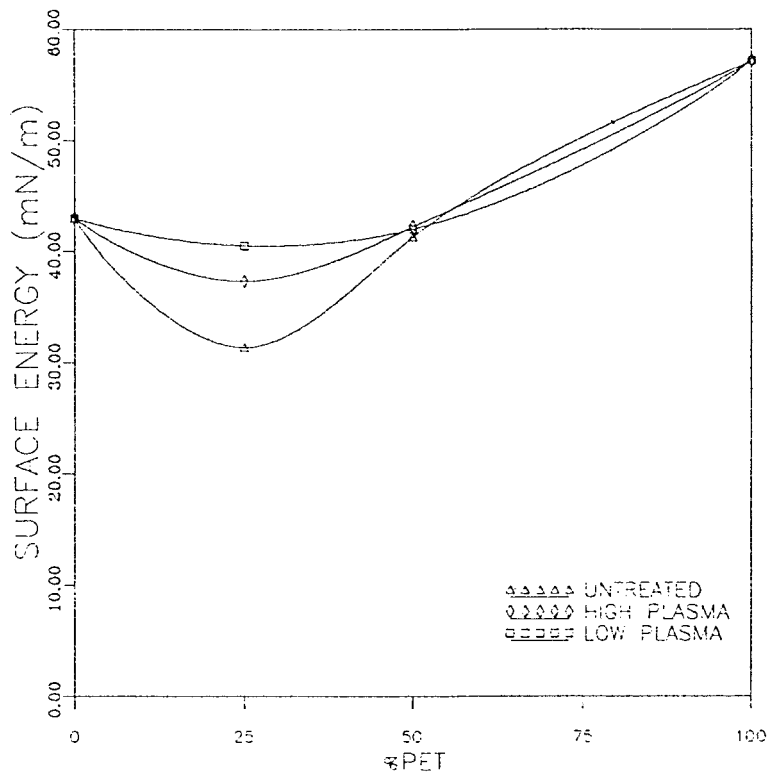
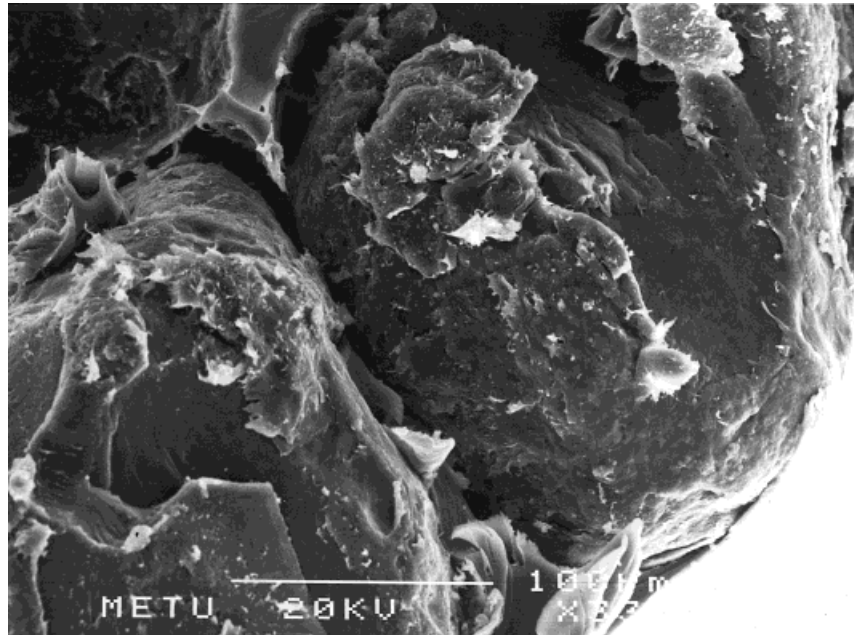
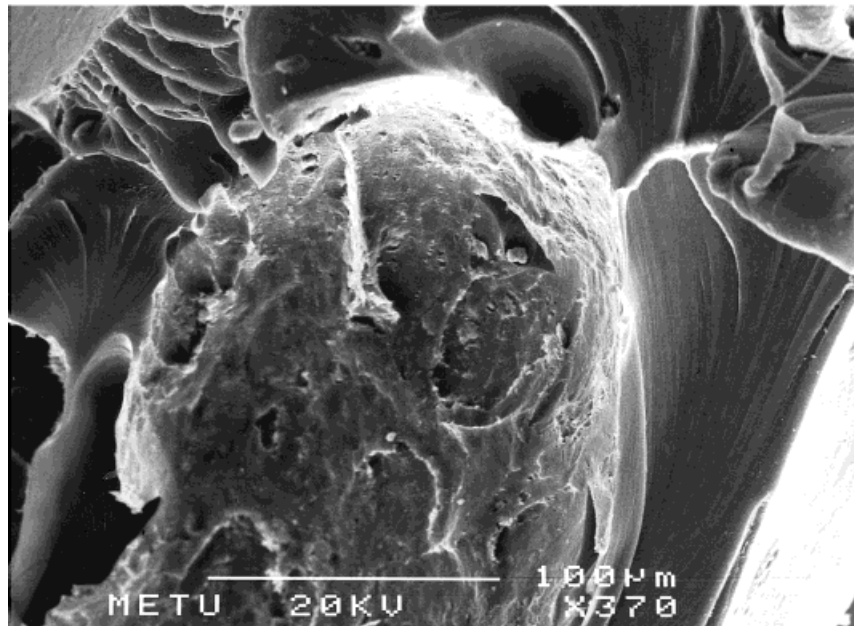


Figure 7 Comparison of different plasma conditions on surface energies for the 25 and 50% DCE plasma-treated PET.



(a)



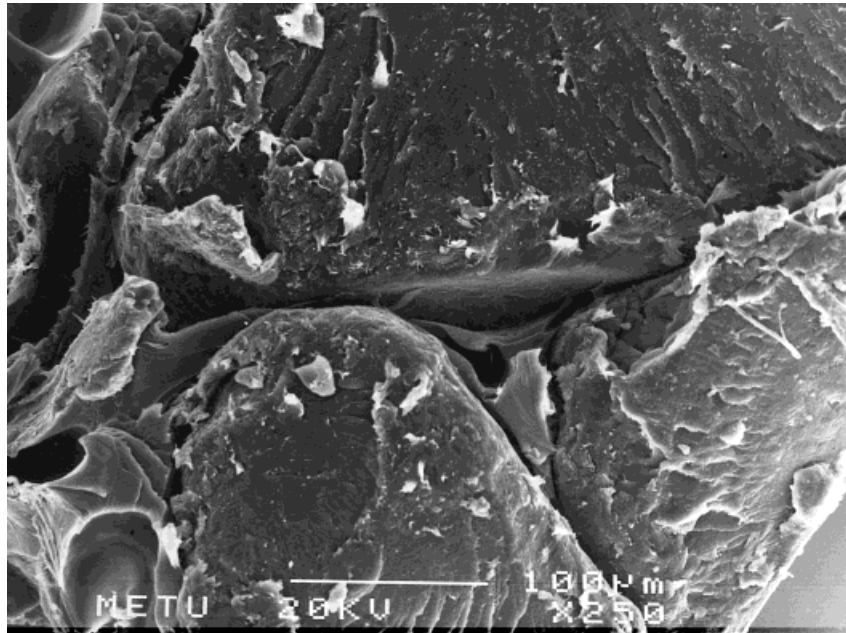
(b)

Figure 8 SEM micrographs of (a) a 25% PET/PVC composite ($\times 330$), (b) the same composition prepared with VCM-treated PET ($\times 370$), (c) a 50% PET/PVC composite ($\times 250$), and (d) the same prepared with VCM plasma-treated PET ($\times 220$).

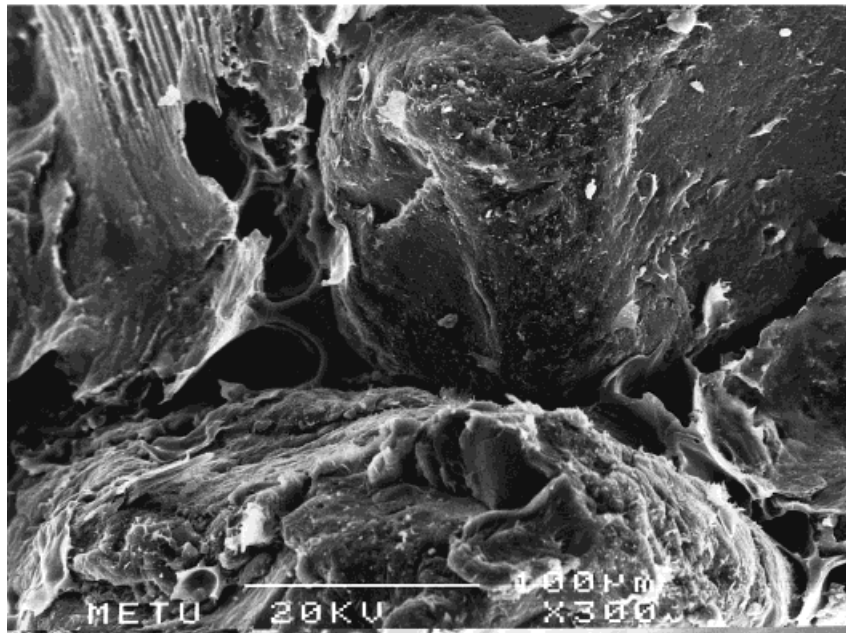
that the mechanical responses and surface energies of samples tested yielded similar parallel results if they are compared for their values versus percent compositions.

SEM micrographs of fracture surfaces of composite samples prepared with 25 and 50% un-

treated and VCM low-plasma-treated PET are presented in Figure 8(a–d), from which it is seen that as a result of plasma application there is not only a plasma (modification) effect expected but also some plasma polymer production on the filler (PET powder) particles.



(c)



(d)

Figure 8 (Continued)

CONCLUSIONS

1. Recycled PET, if powderized and plasma surface-modified properly, can be used in the PVC matrix as the reinforcing filler. The surface modification applied in DCE, TCE, or VC plasma to powdered PET can lead to composite systems with synergetically improved moduli values, even at very high loadings and, hence, to better reinforcements and with improvement in compatibilities.
2. The extrapolation of dilute solution properties to the bulk most probably is not applica-

ble—at least qualitatively and for the conditions studied—and it should not be used to follow the degree of the compatibilities for the PVC system filled with plasma surface-modified PET.

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