

A Compatibility Study of Waste Poly (Ethylene-Terephthalate) with Poly (Vinylchloride)

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SYNOPSIS

Mixtures of PET and PVC were prepared in three different compositions by a solution blending technique. A plasma surface modification method was applied to PET powder surfaces in order to enhance the miscibility of both components because of their mutual insolubility. The intrinsic viscosities of blends were measured in a phenol/tetrachloroethane-mixed solvent system. The degree of compatibility of blends was characterized by the use of the parameter Δb , as derived by Krigbaum and Wall. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Discarded plastic materials, which account for 7–10% (w/w) of all municipal solid waste refuse, cause environmental pollution and draw continuous criticism. Plastic packaging materials form a major part of the plastic waste stream because of their short-term usage, such as PET (polyethyleneterephthalate) and PVC (polyvinylchloride) bottles, which must be recycled, not only for ecological, but also for economical reasons.

A number of plastic recycling methods are already established. The easiest approach for utilization of waste PET and PVC would be the direct blending of these two materials in order to obtain new polymeric systems. However, PET and PVC exhibit a high degree of incompatibility, in addition to the difficulty of preparation of the mixture from the melt. PET has a high melting point (T_m) of 250–260°C and PVC (even if stabilized) decomposes around the T_m of PET. If one considers the use of PET powder as a filler in the PVC/PET composite system, the incompatibility of the components prevents the system from having satisfactory mechanical properties. Hence, it is of interest to modify sur-

faces, interfaces, and/or interphases to enhance compatibility in order to produce better composite systems, which may help to decrease the waste PET–PVC problems in the environment.

For modification of polymer surfaces, to improve adhesion, fluid absorbancy, and wetting properties, “exposure of the surfaces to an electrical corona discharge” method is usually successfully employed,^{1,2} in addition to other chemical modification techniques.³ In this study, low temperature plasma was used to influence and modify interfaces to increase the degree of compatibility.

A viscometric method has been used by several authors^{4–7} to study the interaction of polymers in solution and, hence, to characterize polymer blends for their compatibility. The studies of ternary polymer–polymer–solvent systems are based on the assumption that repulsive interaction may cause shrinkage of the random coils of polymer molecules, which results in the reduction of viscosity below the calculated value, while attractive interaction leads to an increase in viscosity when the system is compatible. The results obtained for liquid solutions can then be extrapolated to the solid state.⁸

In order to analyze the viscosity behavior of ternary systems for interactions, the Krigbaum and Wall⁹ equation has been used:

$$\eta_{sp}c_m = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (1)$$

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where $\eta_{sp,m}$ is the specific viscosity of mixed polymer solution, $[\eta_1]$ and $[\eta_2]$ are intrinsic viscosity of polymer components 1 and 2, C_1 and C_2 are the concentrations of components 1 and 2 in the mixed polymer solution, b_{11} and b_{22} are specific interaction coefficients of components 1 and 2 in single polymer solutions, respectively, and b_{12} is the interaction coefficient for the mixture of components 1 and 2.

The coefficient b_{11} is related to the constant k in the Huggins equation,¹⁰ and can be expressed as follows:

$$b_{11} = k_1[\eta_1]^2 \quad (2)$$

According to Williamson and Wright,¹¹ the interaction coefficient b_{12} can be expressed as:

$$b_{11} = (b_{11} + b_{22})/2 \quad (3)$$

which is our prime interest.

As stated by Krigbaum and Wall⁹ information on the interaction between polymer molecules 1 and 2 can be obtained from a comparison of experimental b_{12} and theoretical b_{12}^* values. The latter value refers to the one computed from eq. (3). Hence, the compatibility of polymer mixtures can simply be characterized by a parameter Δb :

$$\Delta b = b_{11} - b_{22}^* \quad (4)$$

Negative values of Δb are found for solutions of sys-

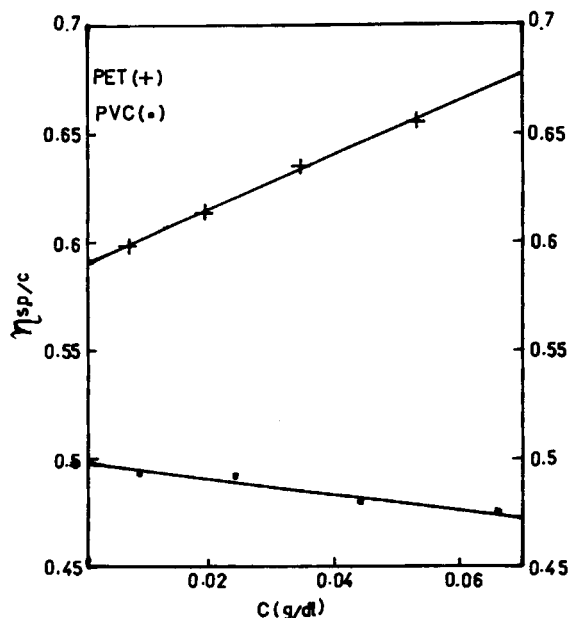


Figure 1 η_{sp}/c vs. c (g/dL) for PET and PVC.

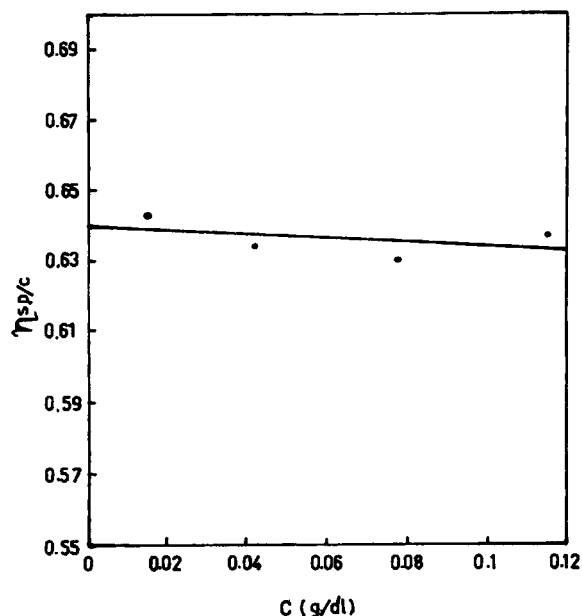


Figure 2 η_{sp}/c vs. c (g/dL) for MPET.

tems with incompatible polymers, while positive values refer to the attractive interactions and compatibility.⁹

EXPERIMENTAL

The PET used in this study was of bottle grade, generated from the processing stage by SASA (Adana), with an intrinsic viscosity of 0.588 dL/g. The PVC, coded as Petvinyl P34/74, supplied by Petkim (Turkish Petro-Chem. Ind. Inc.), was in the form of white powder.

Typical methods for preparing polymer blends cannot be easily employed for PET/PVC blends, due to the high melting point of PET and the instability of PVC (even stabilized) around the melting point of PET. Thus, polymer blends were prepared by the solution-blending method in three different compositions (25, 50, and 75%). Both PET and PVC were dissolved in phenol/tetrachloroethane (1:3) separately. The solutions were then mixed at room temperature and were coprecipitated with methanol (methanol was distilled before use). The precipitate was washed several times with methanol in order to remove the solvent. The blend was then dried under vacuum at 80°C to constant weight.

The modification of PET powder surface was carried out by passing VC (vinyl chloride) gas through the reactor during the plasma.

A 13.56 MHz radiofrequency glow discharge re-

actor, with a maximum output of 100 W, was employed in this study. After the placement of the sample in the reactor, the reaction chamber was flushed with VC gas and the glow discharge was sustained in a continuous flow for 15 min at 10 W.

The specific viscosities of the polymers and their mixtures were determined by an Ubbelohde-type Automatic Viscometer, in phenol/tetrachloroethane solution, at 25°C. A Perkin-Elmer System 4 Differential Scanning Calorimeter was used for thermal analysis. Surface Morphologies were examined by Scanning Electron Microscopy (SEM) studies.

In some experiments, PVC was further purified with methanol extraction for 2 h by use of a soxlet apparatus, and these samples are labelled as "extracted PVC."

RESULTS AND DISCUSSION

Equation (1), derived by Krigbaum and Wall, depends on the molecular weight of the studied polymers for validation. It has been shown that for polymers with a molecular weight of about 100,000, the equation is valid up to a concentration of 2.0 g/dL. The highest concentration used in this study was 0.06 g/dL.

Figures 1 and 2 show the intrinsic viscosity values vs. c for PET, PVC, and for plasma modified PET (MPET).

The slopes that refer to interaction coefficient b , for each component in a single polymer solution and intercepts, are obtained by the least square method and are presented in Table I. The slight increase in the intrinsic viscosity of MPET is probably due to the production of some crosslinks, as a result of subsequent reactions of free radicals formed at the surface during plasma application.

Table II presents the intrinsic viscosities of polymer mixtures with different compositions that were studied, while Figure 3 shows the plot of the intrinsic viscosity vs. percent compositions for the blends tested. The straight lines represent ideal solutions. As seen in Table II, which describes both the PET/

Table I $[\eta]$, r , and b Values for PET, PVC, and MPET

Polymer	$[\eta]$	r	b
PET	0.588	0.999	1.34
PVC	0.498	-0.97	-0.356
MPET	0.645	0.958	0.205

Table II Intrinsic Viscosities of the Polymer Mixtures Studied

Blend	PET (wt %)	$[\eta]$	r
PET/PVC	25	0.37	0.99
	50	0.752	0.92
	75	0.614	-0.97
MPET/PVC	25	0.588	0.966
	50	0.613	0.99
	75	0.536	0.92

PVC and MPET/PVC mixtures, considerable deviation from the ideal was observed. However, the compositions obtained using of MPET showed behavior that was much closer to the ideal, as compared with that of PET.

Δb of Mixtures

PET/PVC Mixtures

The values of Δb , according to eq. (1), were computed for different total concentrations of PET/PVC mixtures and are shown in Figure 4.

It is evident that Δb decreases as the total concentration of the mixture decreases. This is probably due to an increase in the interaction between solvent and polymers as the solvent concentration increases. The values of Δb are negative at all mixture compositions and concentrations. It was found that the value of Δb decreases (more negative) as the amount of PET increases in the mixture. These results suggest that the PET/PVC blend system becomes more incompatible as the amount of PET increases in the mixture.

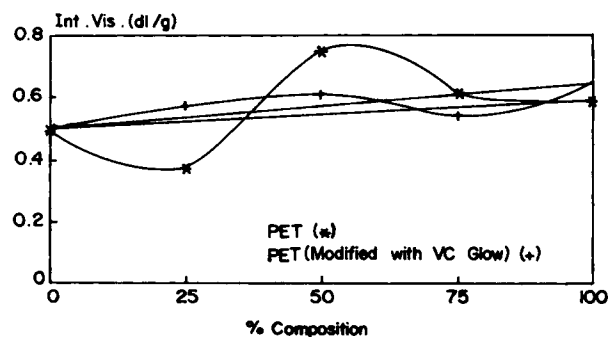


Figure 3 $[\eta]$ vs. % composition for the PET/PVC and MPET/PVC systems.

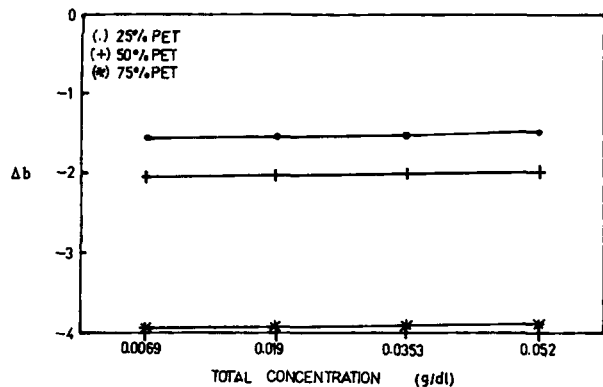


Figure 4 Δb vs. total concentration for PET/PVC mixtures.

MPET/PVC Mixtures

The values of Δb vs. the total concentration for the MPET/PVC blend systems are shown in Figure 5. When Figure 4 is compared to Figure 5, it can be seen that the MPET showed less negative Δb values from an increase in the interaction between PET and PVC. A decrease in Δb values was also observed for these blend systems as the amount of the MPET was increased in the mixture when compared at the same concentration. It has been found that the Δb values of 25% and 50% MPET mixtures show nearly the same Δb values.

It is always of interest to learn the extent of compatibilization in blend systems. To gain insight, the variation of T_g values of PET, MPET, and PVC with % composition PVC, in a series of PET/PVC and MPET/PVC blend systems, were obtained experimentally. Results were presented in Figure 6 in the form of T_g values vs % PVC in the blend system studied. From the plot, for PET and MPET, completely different trends are observable. There is a

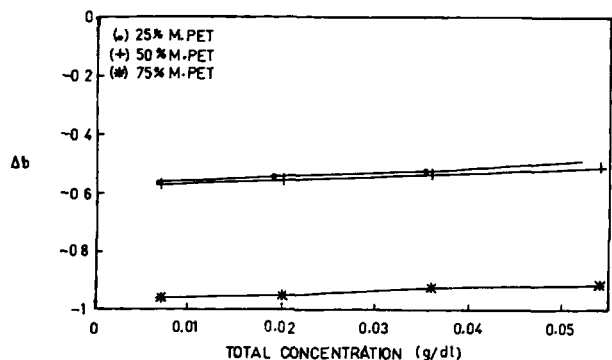


Figure 5 Δb vs. total concentration for MPET/PVC mixtures.

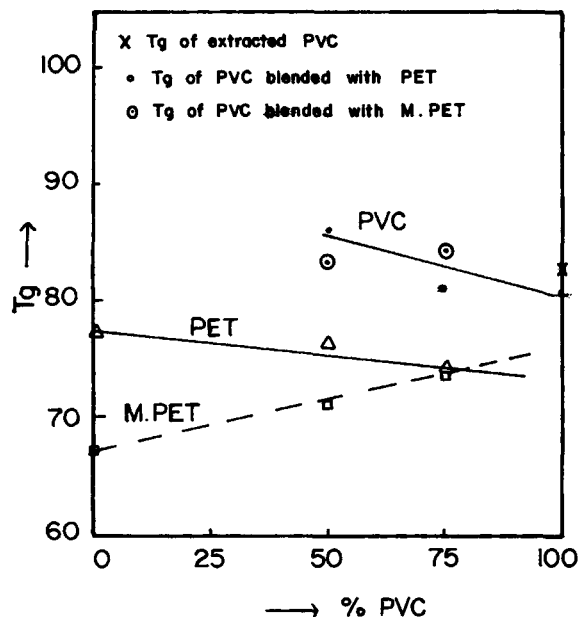


Figure 6 T_g vs. % composition for mixtures.

regular increase in the case of MPET, while in the case of PET, it is just the reverse. Considering the higher T_g of PVC, an increase in the T_g of MPET is expected if more PVC molecules are thought to be forced to enter the MPET regions, (i.e., an increase in compatibility). Meanwhile, the T_g of PVC will not change. The sharp drop in the T_g of PET upon modification is open to speculation, and it is probably due to the production of oligomers during the plasma process in addition to surface modification species. PET is sensitive to impurities and

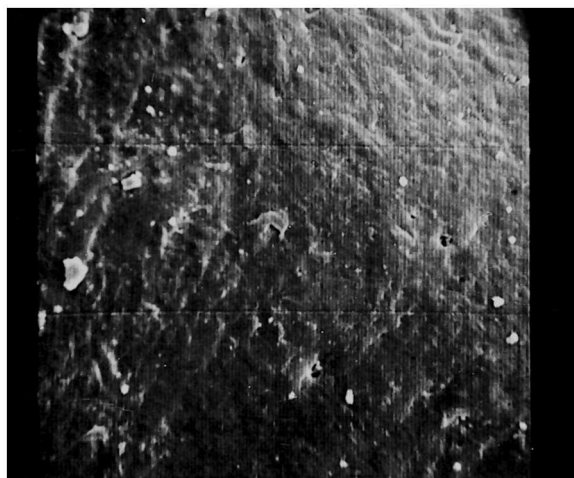


Figure 7 Micrograph of PET.



Figure 8 Micrograph of MPET.

probably, after the diffusion of these impurities into amorphous PET, plasticization occurs. For the opposite trend, however, one can think of the effect of impurities existing in PVC. In fact, this has been proved by repurification of PVC in a soxlet apparatus, which yielded a higher T_g value for PVC.

The 75% PET and 75% MPET containing blends could not be produced and hence no DSC data was available for them.

Scanning Electron Microscopy (SEM) photographs have been used in order to check the appearance of both polymers alone and their mixtures. Figures 7 and 8 show the micrographs of PET and MPET with the same magnification value ($\times 1600$).

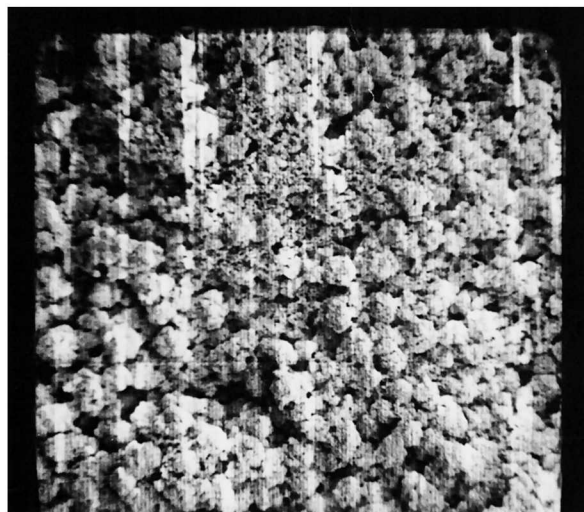


Figure 9 Micrograph of 50% PET, 50% PVC.

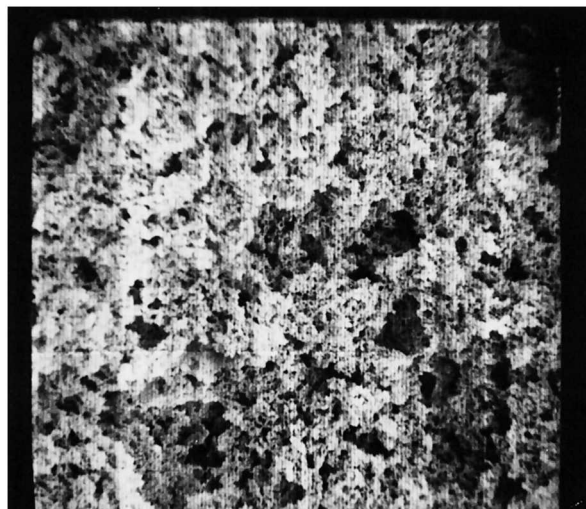


Figure 10 Micrograph of 50% MPET, 50% PVC.

These micrographs do not show appreciable differences, except the latter one, with some traces of deposit production due to the plasma.

The micrographs of 50% PET, 50% PVC and 50% MPET, 50% PVC blends show consistent results with the Δb parameters, obtained from the viscosity measurements (Figs. 9 and 10). As it is observed from these figures, the surface texture of the 50% PET/PVC mixture has a coarser appearance, as compared with that of the 50% MPET/PVC.

CONCLUSION

1. Although the number of PET bottles is fewer than others, it is still one of the most important sources in the plastic waste stream, because it is immediately added to the plastic waste stream after use. Since plastic wastes need to be sorted after collection, a PET/PVC blend could be an alternative material that would reduce the cost of recycling.
2. The $[\eta]$ vs. % composition diagram has shown that the modified PET has increased interaction with PVC. So "Plasma Glow Discharge" could be a method to increase the compatibility between immiscible polymers.
3. The previous result has also been deduced by a parameter Δb , derived by Krigbaum and Wall. Thus, a simple viscometric technique is useful in studying polymer compatibility as a measure of solid state compatibility.

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