

Recycling of PET and PVC Wastes

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Received 15 July 1996; accepted 31 May 1997

ABSTRACT: A method for recycling mixed PET and PVC wastes is described. Glycolysis of PET leads to oligomers that are polycondensed with caprolactone. The obtained diols are extended with hexamethylene diisocyanate. In certain conditions the polyurethanes are totally miscible with PVC, leading to acceptable mechanical characteristics for the blend. A relation between the structure of the polyurethane and miscibility with PVC is described. The mechanical characteristics of the blend depends on the polyurethane chemical structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 657–665, 1998

Key words: PVC; PET; recycling; glycolysis

INTRODUCTION

PET and PVC wastes are a potential source for recycling applications. However, there are technical difficulties in obtaining a final product with acceptable mechanical properties. When collected together, the major issue is to sort out the two polymers to treat them separately. Unfortunately, PET and PVC separation is not easy using simple and inexpensive methods such as the difference of density of the two polymers. Sorting out the two polymers by using a spectroscopic method adds an extra cost to the treatment. The aim of our project was to find a method that avoids the sorting steps so that the wastes could be treated directly after the collecting steps.

Recycling processes for PET alone do exist. When the PET is blended with PVC, this is difficult. These polymers are chemically incompatible and their processing temperatures are different. These features lead to different situations, depending on the blend composition. PVC contaminated with a small amount of PET can be trans-

formed at temperatures ranging from 160 to 190°C. In this case, PET behaves as a charge within the PVC matrix. However, PET contaminated with a small amount of PVC is impossible to treat by a common transformation method such as extrusion or injection. PVC degrades at the PET transformation temperature, leading to a material with unacceptable mechanical characteristics.

PET recycling has become common in the industry. Different processes are available and most of them consist of esterifying the polyester with an excess of reactant such as diols, diamines, alcohols, or water. PET conversion products are used as monomers for further synthesis of PET, polyurethanes (PUs), or polyesters. Table I summarizes the most popular methods to treat PET wastes.

We planned to treat PET/PVC blends as we treat PET alone. The second step of the process consists of polycondensing the depolymerization products of PET with a reactant to obtain a new polymer compatible with PVC. The reactant we chose was ϵ -caprolactone because of the miscibility of its homopolymer with PVC.³² Aubin and Prud'homme³³ studied the miscibility of PVC with several polylactones and pointed out the mono-

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Journal of Applied Polymer Science, Vol. 69, 657–665 (1998)

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CCC 0021-8995/98/040657-09

Table I Common PET Depolymerization Treatments for Recycling

Treatment	Reactant	Reaction Products	References
Alcoholysis	EG	BHET and EG	1–21
Hydrolysis	Water	Terephthalic acid and EG	22–25
Methanolysis	Methanol	Dimethyl terephthalate and EG	26–28
Aminolysis	Amine	Terephthalamide	29–31

EG, ethylene glycol; BHET, bishydroxyethylterephthalate.

phasic structure of the blends. They noticed only one glass transition temperature, whatever the composition of the blend was. This temperature increases gradually with the composition.

EXPERIMENTAL

PET Depolymerization

PET (40 g, Arnite A from Akzo Chemical), 66 g of ethylene glycol (EG), and 0.53 g of zinc acetate were mixed and heated to 190°C for 6 h in a three-necked flask equipped with a condenser and a stirrer. After cooling the mixture was mixed in 1 L of water and filtrated. The white residue was dried under a vacuum at 80°C for 24 h.

Synthesis of Co-oligomers 1/1, 1/3, and 1/5

PET depolymerization products [0.05 mol, bishydroxyethylterephthalate (BHET) and dimer], 0.05*n* mol (*n* = 1, 3, or 5) of ϵ -caprolactone, and 0.1 wt % of dibutyltin dilaurate (DBTDL) were mixed and heated to 150°C for 2 h in a three-necked flask equipped with a condenser and a stirrer.

Synthesis of PUs PU1/1, PU1/3, and PU1/5

The co-oligomer (0.01 mol) was dissolved in 500 mL of tetrahydrofuran (THF) in a three-necked flask equipped with a condenser and a stirrer. The temperature was raised to 67°C and a solution of 0.01 mol of hexamethylene diisocyanate (HMDI) in 50 mL of THF was added dropwise. After 12 h the mixture was cooled and precipitated in ether. The precipitate was isolated by filtration and dried at 70°C for 12 h.

Preparation on PVC/PU Blends

The blends were prepared by dissolving the two components in THF and coprecipitating in ether.

The precipitate was washed with ether and dried at 70°C for 12 h.

Preparation of ISO 1/2 Specimens for Mechanical Properties Analysis

The blends were compression molded at 130°C under pressure (200 bar) and cut into ISO 1/2 test bars. They were tested on an INSTRON 1/195 apparatus.

SEM Analysis

A specimen was broken in liquid nitrogen, and the surface fracture was observed using a Cambridge Stereoscan 260 microscope.

Mechanical Analysis

When the ISO 1/2 specimens were tested on the Instron 1/195, a crosshead speed of 50 mm/mn was used to determine the breaking strength (confidence limit of 0.5 MPa) and the elongation at break (confidence limit of 1%).

RESULTS AND DISCUSSION

The first part of the work consisted of studying the depolymerization of PET and the polycondensation of its reaction products with ϵ -caprolactone. We decided to model the process and characterize the reaction products for each step of the process. In the first step we studied PET depolymerization.

A more realistic run was made at the end of the study with the two components of the blend during all the process stages. Obtained materials were characterized by proton NMR analysis and SEM, and their mechanical properties were determined.

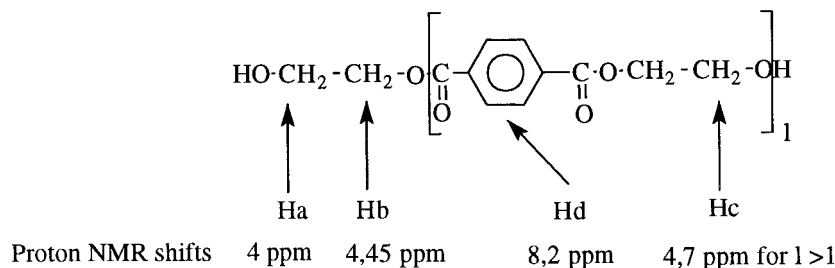


Figure 1 Chemical structure and proton NMR chemical shifts of PET oligomer.

PET Depolymerization

Experimental conditions were according to Baliga and Wong.¹ PET was depolymerized with an excess of EG, and zinc acetate was the catalyst. The reaction was carried out at 190°C for 6 h. The EG excess was eliminated by washing with water, and the remaining products were dried and characterized by proton ¹H-NMR analysis. There was 80 wt % BHET (1 = 1) and 20% dimer (1 = 1). This result was in accordance with Baliga and Wong's results of 15% of the dimer (Fig. 1).

Condensation of Depolymerization Products of PET with ϵ -Caprolactone

To simplify the reaction scheme, we decided to work with BHET only. The dimer was isolated by precipitation in hot water (90°C) and filtration.

BHET was condensed with ϵ -caprolactone at 150°C using DBTDL as the catalyst. We varied

the quantity of ϵ -caprolactone to obtain three different co-oligomers. We called them 1/1 (1 mol BHET for 1 mol ϵ -caprolactone), 1/3 (1 mol BHET for 3 mol ϵ -caprolactone), and 1/5 (1 mol of BHET for 5 mol ϵ -caprolactone) (Fig. 2).

The reaction was monitored by gel permeation chromatography analysis. Once the ϵ -caprolactone was totally consumed the reaction was stopped (2 h). The three products were characterized by proton ¹H-NMR analysis, and the average polymerization degree was calculated by comparing the integration signals of the α -hydroxymethylene groups with the α -carboxymethylene groups. The results are displayed in Table II.

Synthesis of PUs Using ϵ -Caprolactone/BHET Co-oligomers

Co-oligomers 1/1, 1/3, and 1/5 were extended with HMDI (1 mol HMDI for 1 mol co-oligomer).

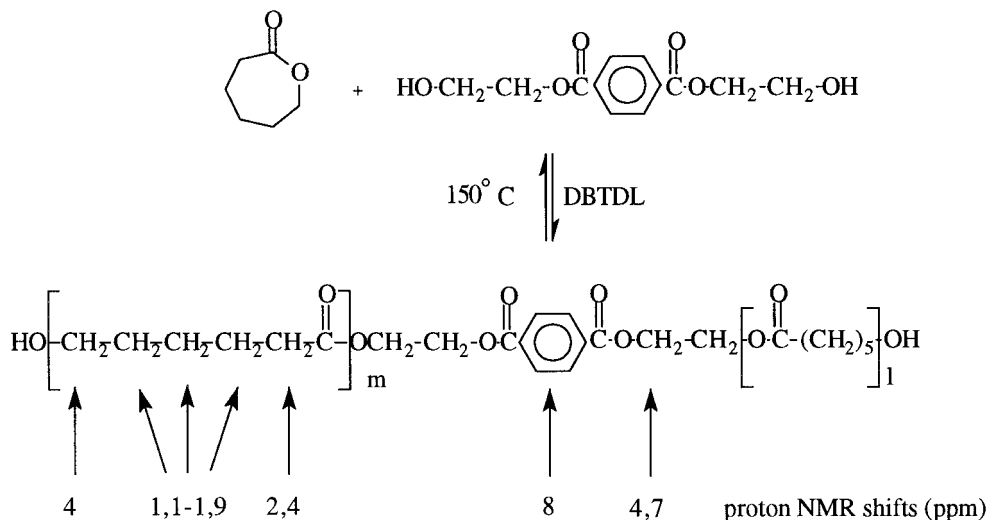


Figure 2 Co-oligomer's synthesis reaction scheme.

Table II Co-oligomer's DP_n

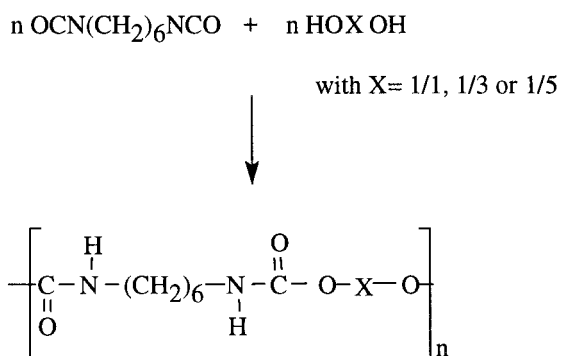
Product	$DP_n(l + m)$	
	Theor	Calcd
1/1	1	1.2
1/3	3	3.3
1/5	5	4.8

The hydroxyl content of the co-oligomers was calculated from the average degree of polymerization (\overline{DP}_n) determined by proton $^1\text{H-NMR}$ analysis. The obtained PUs were PU1/1, PU1/3, and PU1/5. The reaction was monitored by FTIR analysis. The total disappearance of the isocyanate vibration band at 2250 cm^{-1} indicated the end of the reaction (Fig. 3).

The PUs were compression molded after melting. Their mechanical characteristics are displayed in Table III. As expected, increasing ϵ -caprolactone content in the polyurethane decreased the breaking strength and increased the elongation at break. The higher the concentration of the urethane groups is, the harder the material is. Increasing ϵ -caprolactone content decreased the urethane group concentration, leading to a softer material.

Mechanical Properties of PVC/PU Blends

The blends were prepared by dissolving the PUs and PVC in THF and coprecipitating in ether. After drying, the blend was compression molded and ISO $\frac{1}{2}$ test bars were cut. The mechanical behaviors of the blends are displayed in Figures 4 and 5. We tested three compositions: 25% PU + 75% PVC, 50% PU + 50% PVC, and 75% PU

**Figure 3** Polyurethane's synthesis reaction scheme.**Table III** Mechanical Characteristics of PU1/1, PU1/3, and PU1/5

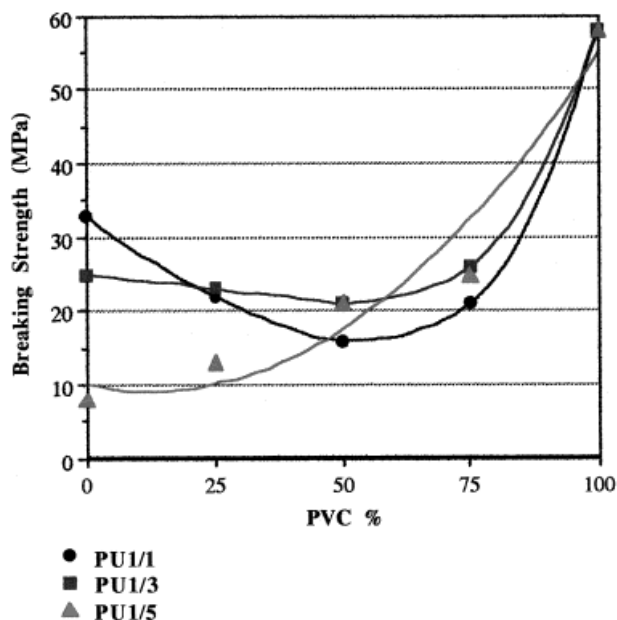
	Breaking Strength (MPa)	Elongation at Break (%)
PU1/1	32	900
PU1/3	25	> 1000
PU1/5	9	> 1000

+ 25% PVC. The mechanical analyses pointed out that the characteristics of the blends depends on the chemical structure of the PU. We note that increasing the ϵ caprolactone content of the co-oligomer softened the blend. The elongation at break increased and the breaking strength decreased.

DSC Analysis of Blends

The DSC analyses of the blends highlight the glass transition temperatures of the blends. The results are displayed in Figures 6, 7, and 8 for PVC/PU1/1, PVC/PU1/3, and PVC/PU1/5 blends, respectively.

Two different behaviors were noted. PU1/1 and PU1/3/PVC blends exhibited two glass transition temperatures whatever the composition was. PU1/5/PVC blends exhibited only one glass tran-

**Figure 4** Breaking strength of PVC/polyurethane blends.

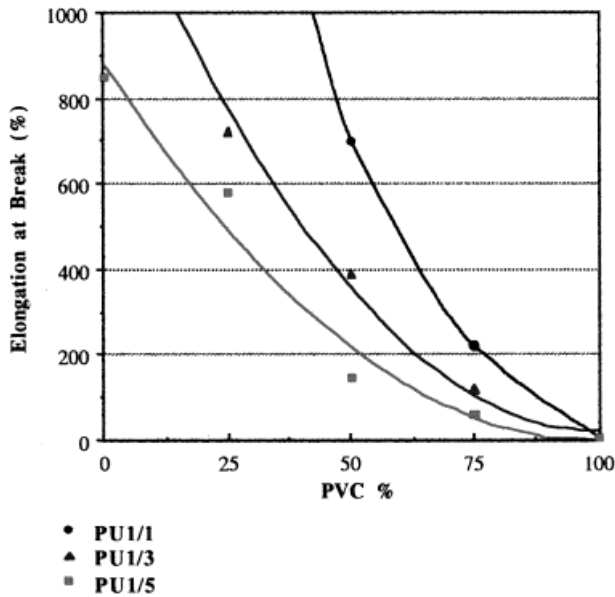


Figure 5 Elongation at break of PVC/polyurethane blends.

sition temperature whatever the composition was. We concluded that only PU1/5 is miscible with PVC. We applied the calculation of glass transition temperature for a miscible blend to the PU1/5/PVC blend:

$$\frac{1}{T_g} = \frac{w_a}{T_{ga}} + \frac{w_b}{T_{gb}}$$

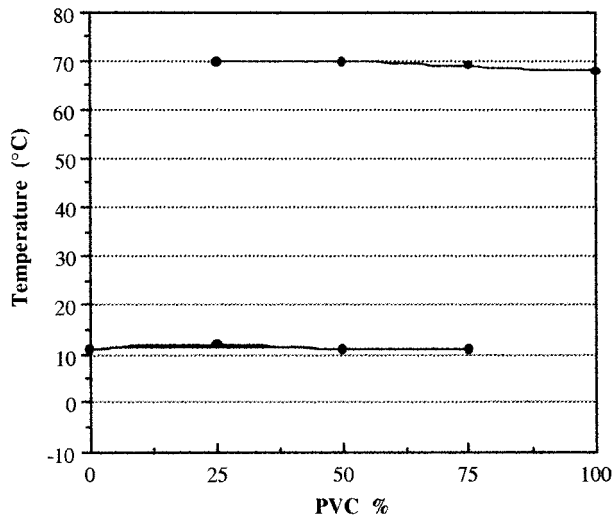


Figure 6 Glass transition temperatures of PVC/PU1/1 blends.

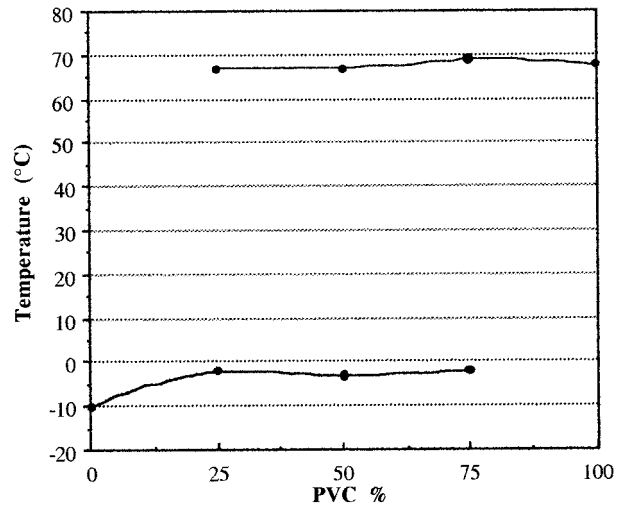


Figure 7 Glass transition temperatures of PVC/PU1/3 blends.

where w_a is the weight fraction of component A, w_b the weight fraction of component B, T_g the glass transition temperature of the blend, T_{ga} the glass transition temperature of component A, and T_{gb} the glass transition temperature of component B.

The comparison between theoretical and experimental results are displayed in Figure 9. We were in accordance with the theoretical calculation with an error of 10°C. The glass temperature evolution was quasilinear with the composition.

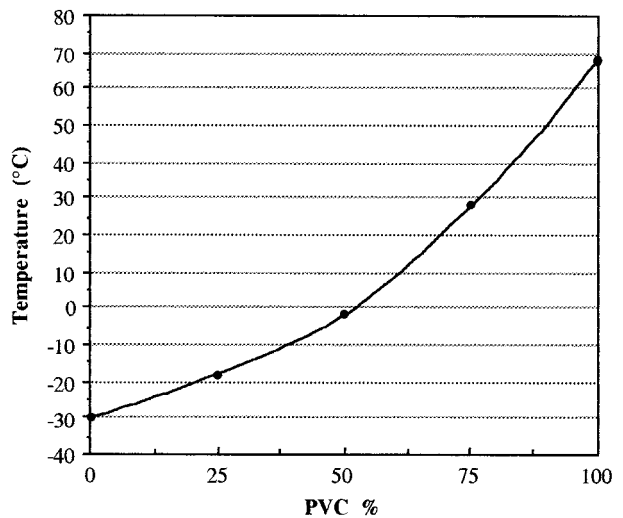


Figure 8 Glass transition temperatures of PVC/PU1/5 blends.

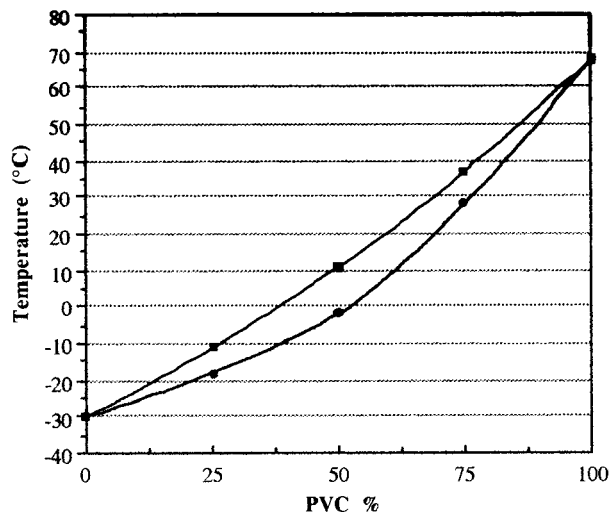


Figure 9 (●) Experimental and (■) theoretical glass transition temperatures for PVC/PU1/5 blend.

SEM of 50/50 PVC/PU Blends

The surface fracture observations of the blends showed the structure of the materials. The PVC/PU1/1 and PVC/PU1/3 blends exhibited a biphasic structure; the phase size decreased from the PVC/PU1/1 to the PVC/PU1/3 blend (Figs. 10, 11) that became monophasic for the PVC/PU1/5 blend (Fig. 12).

The set of analyses we performed reveals that we are in total agreement with Woo et al.³⁴ who proposed a relation between carbonyl functions concentration to explain the miscibility phenomena of PVC with various polyesters. In our case, increasing ϵ -caprolactone content in the co-oligomer increased the carbonyl concentration in the blend and led to a PU that was miscible with PVC. This was demonstrated by the DSC analyses and the SEM analyses. Moreover, the energy dispersive analysis performed during the SEM observation revealed that the chlorine content was varying from phase to phase for PVC/PU1/1 and PVC/PU1/3 blends but was constant on the overall surface of the PVC/PU1/5 sample.

The miscibility phenomena is explained by Woo et al.³⁴ who noticed a relation between miscibility and structure of the aliphatic polyester. Miscibility is directly related to the number of interactions between carbonyl groups of the polyester and α hydrogens of PVC. They pointed out that aliphatic polyesters having a ratio of $\text{CH}_2/\text{COO} < 4$ are not completely miscible with PVC. When this ratio is between 4 and 10 they noted a complete miscibility with PVC. We calculated the ratio CH_2/COO to verify Woo et al.'s findings. The results are displayed in Table IV. We observed that, considering both urethane and carbonyl groups in the calculation, there is a strong relation between the miscibility of the

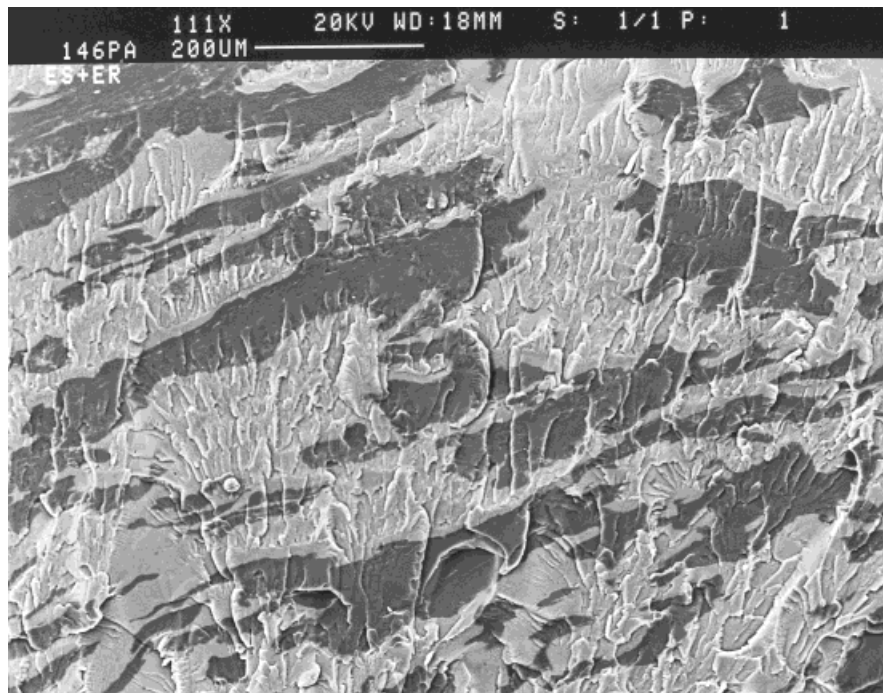


Figure 10 Surface fracture observation of 50PVC/50PU1/1 blend ($\times 111$).

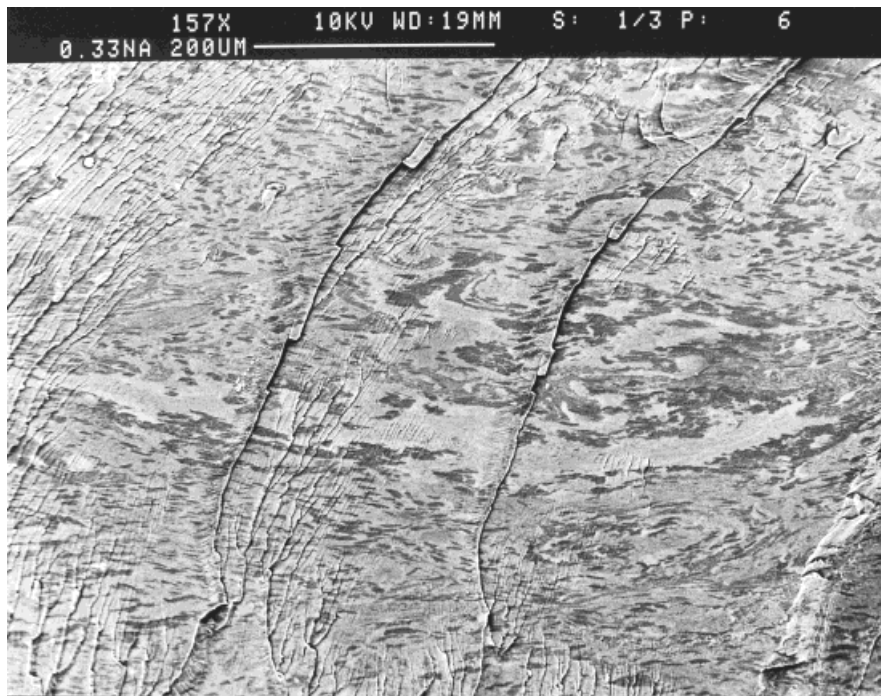


Figure 11 Surface fracture observation of 50PVC/50PU1/3 blend ($\times 157$).

blend and the number of polar chemical functions within the PU. We were very close to a ratio of 4 when the miscibility phenomena occurred. The

study of Woo and colleagues was about aliphatic polyester. In our case aromatic rings interfered, but our results are quite similar to theirs.³⁴



Figure 12 Surface fracture observation of 50PVC/50PU1/5 blend ($\times 526$).

Running Process Using PET/PVC Wastes

The process was run in the same way as above for the PU1/5 synthesis, even for the glycolysis of PET. The difference was that PVC was present at all stages of the process. The issue was to keep it from degrading during the PET depolymerization step. The temperature was raised to 190°C during 6 h in EG as the reactive solvent. We used a blend of 85% PVC and 15% PET from bottle wastes, and we did not notice a drastic thermal degradation of PVC during the process. The mechanical behavior of the end material was the same as the one we did (for the same proportion of PVC) during the model study, even if the PET and PVC were not the same. The mechanical behavior of the obtained product was compared to the corresponding material from the model study (Table V).

CONCLUSION

The process we described above reveals that it is possible to obtain materials with acceptable mechanical characteristics from PET/PVC wastes. We observed that the behavior of the PVC/PU blend is strongly dependent on the ϵ -caprolactone concentration used for the co-oligomer synthesis. We noted that the blend exhibits two types of behavior regarding its composition. Only PU1/5 is perfectly miscible with PVC. This is demonstrated by the DSC analysis (Fig. 5) that shows the monophasic structure of the material with one glass transition temperature. Decreasing the ϵ -caprolactone quantity in the co-oligomer leads to PUs (PU1/1 and PU1/5) that exhibit a biphasic structure. This can be observed in Figures 6 and 7, where two glass transitions are reported whatever the composition of the blends is. The microscopic observation of surface fractures of the blends confirms the biphasic structure for the

Table IV CH₂/(COO and CON) Content of Co-oligomers and Polyurethanes

	Glass Transition Temperatures	CH ₂ /(COO and CON) Ratio
1/1	—	3
1/3	—	3.8
1/5	—	4.14
PU1/1	2	3
PU1/3	2	3.57
PU1/5	1	3.88

Table V Mechanical Characteristics Comparison Between Products Obtained from Model Study and Products Obtained with PVC/PET Wastes

	Model Study	Real Case
Breaking strength (MPa)	21.1	21.7
Elongation at break (%)	730	450

PVC/PU1/1 and PVC/PU1/3 blends (Figs. 9, 10) and the monophasic structure of the PVC/PU1/5 blend (Fig. 8).

The mechanical characteristics of the blends reveals the importance of the chemical structure of the co-oligomers. Increasing the ϵ -caprolactone content leads to a softening of the material with an increase of the elongation at break. Figures 7 and 8 show the mechanical behavior difference for the three blends. Increasing ϵ -caprolactone content leads to elastomeric materials. The mechanical characteristics of the blend can be adjusted by varying the chemical structure of the co-oligomer and the amount of PU in the blend. This can be of great interest for modifying the material characteristics in regard to the application needed. Different reactants could be used for the synthesis of the co-oligomers and the PUs. Changing the diisocyanate or the ϵ -caprolactone enlarges the number of possibilities.

The work we described is a chemical plastic recycling process for PVC/PET blends that can find application when sorting operations are not possible or too expensive. The advantage of the process is its ability to adapt the end product mechanical characteristics according to the application needed. Although the approach is innovative, the energy and material economics needs some attention. Moreover, the feasibility of melt blending will be investigated. These two points will be presented in our future publication.

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