

Chemical Modification of Virgin and Recycled Poly(ethylene terephthalate) by Adding of Chain Extenders during Processing

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ABSTRACT: The processing of recycled poly(ethylene terephthalate) (PET) involves thermal and hydrolytic degradation of a polymer, which reduces the molecular weight, the intrinsic viscosity, and the mechanical properties of recycled materials. Degradative effects can be limited by using chain extenders. Preliminary tests show that the diisocyanates are more reactive toward the end groups of virgin PET than are bis-oxazolines or diepoxides under the experimental conditions used. So, samples of modified virgin PET with diisocyanates possess molecular weight and intrinsic viscosity ($M_w > 60,000$ g/mol and $[\eta] > 1$ dL/g) superior to those of virgin PET ($M_w > 40,000$ g/mol and $[\eta] > 0.70$ dL/g). Chemical modification of recycled PET by diisocyanates leads to an increase in the molecular weight from 30,000 to 51,000 g/mol, the intrinsic viscosity from 0.60 to 0.84 dL/g, and the mechanical properties, particularly the elongation at break, from 5 to 300%. Chemical modification of recycled PET by injection molding is an interesting method from an industrial point of view because it provides a recycled material possessing properties close to virgin PET in one-step processing. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1816–1824, 2001

Key words: virgin poly(ethylene terephthalate); recycled poly(ethylene terephthalate); chain extenders; chemical modification; intrinsic viscosity; mechanical properties

INTRODUCTION

Poly(ethylene terephthalate) (PET) recycling is currently in a growing stage of development because this polymer is widely used in the manufacture of fibers, beverage bottles, and photographic supports. The thermal and hydrolytic degradation of recycled PET caused by the simultaneous presence of retained moisture coming from the shape of particles and the contaminants

(PVC, adhesives, etc.) generates some problems^{1–5} associated with the loss of molecular weight which leads to a decrease in the intrinsic viscosity.⁶ The decrease in these two parameters affects the mechanical properties of recycled material. The reduction in the chain length of PET caused by degradative chain scission can, in part, be compensated for by the use of a chain extender. Those are polyfunctional compounds, thermally stable and capable of fast reactions with the hydroxyl or carboxyl end groups of PET in a nearly irreversible manner under normal process conditions. Some examples of chain extenders cited in the literature^{7–14} are diepoxides, diisocyanates,

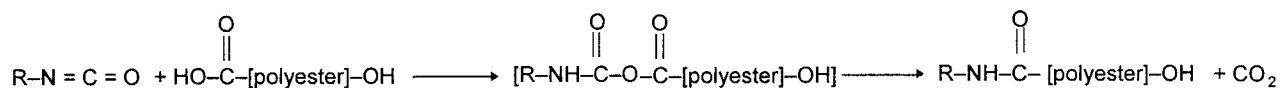
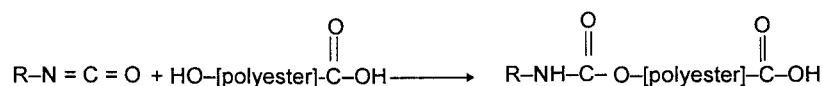
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dianhydrides, bis-oxazolines, carbodiimides, and bis-dihydrooxazines.

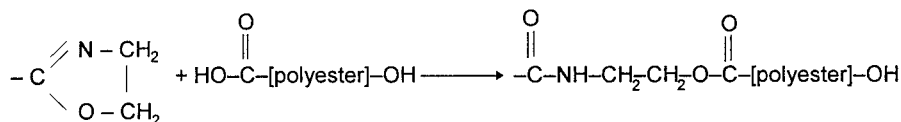
To modify chemically virgin PET, chain extenders used are as follows:

- Diisocyanates, which react with hydroxyl (preferentially) and carboxyl end groups of PET. In the first case, there is formation of urethane groups, and in the second case,



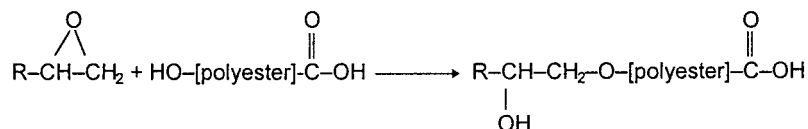
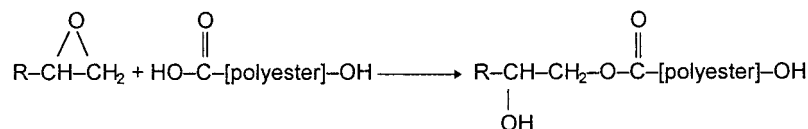
- Bis-oxazolines, which possess a high reactivity toward carboxyl groups¹⁵ and lead to the formation of stable esteramide linkages. Kinetic studies¹⁶ performed by ultraviolet and

infrared spectroscopy showed that the reaction between oxazoline and carboxylic acid is fast (3–5 min) at 185°C:



- Diepoxides react with carboxyl (preferentially)

and hydroxyl end groups of PET to form esters:



All these reactions are classic in organic chemistry but they must be adapted to short residence times and high temperatures in the range 260–280°C.

Among the chain extenders used, we chose diisocyanates to modify recycled PET. This work consisted of studying the torque, intrinsic viscosity, molecular weight, and mechanical properties (Young's modulus, elongation at break, and impact

strength) of modified virgin and recycled PET with chain extenders. The originality of this work is that it provides a way for a chemical modification of virgin and recycled PET directly by injection molding and the study of mechanical properties of these materials. This melt processing is very interesting from an industrial point of view because it proves that modified recycled PET with good mechanical properties can be obtained in one-step processing.

Table I Chemical Structures of Chain Extenders

Chain Extenders	Chemical Structures
4,4'-Methylene-bisphenylisocyanate (MDI) (pellets, purity > 98%, Aldrich)	
Hexamethylenediisocyanate (HMDI) (liquid, purity > 98%, Aldrich)	$O=C=N-(CH_2)_6-N=C=O$
Phenylene bis-1,4-oxazoline (powder, purity > 97%, Interchim)	
2,2'-Bis-oxazoline (powder, purity > 97%, Interchim)	
Bisphenol A diglycidyl ether (DGEBA) (viscous liquid, purity of 90%, Lancaster)	

EXPERIMENTAL

Materials

Two types of materials were used in this study: Virgin PET (PETV) was supplied by Akzo Nobel Chemicals (Belgium) (MO3-300) and was a bottle-grade material with an intrinsic viscosity of 0.76 dL g^{-1} . Scraps of recycled PET (PETRc) came from heterogeneous deposits of various color post-consumer bottles and contained 6000 ppm of PVC.

The chemical structures of the chain extenders used in this study are shown in the Table I. Poly(ethylene glycol)monomethyl ether (PEG) of a number-average molecular mass of 550 g/mol was purchased from the Aldrich Chemicals Company.

Melt Processing

Pellets of virgin PET and scraps of PETRc were dried under a vacuum for 12 h at 120°C . The reaction of chain extension was carried out in a Rheocord Haake mixer (50 cm^3). MDI or phenylene bis-1,4-oxazoline or 2,2'-bis-oxazoline were introduced when the polymer is molten. With HMDI or DGEBA being liquid, they were introduced with the polymer in the preheated

batch mixer. PETV or PETRc (50 g) and the chain extender (0.45 g) were mechanically mixed at 64 rpm for 5 min at 270°C . A sampling of the material in the molten state was made after 2 min of mixing.

PETV with 0.9 wt % HMDI or PETRc with 0.9 wt % HMDI were injection-molded into the shape of ISO 1 test bars with a BILLION 90-ton injection-molding machine. Typical molding conditions are as follows:

- Barrel temperature: $250\text{--}280^\circ\text{C}$;
- Mold temperature: 16°C ;
- Overall cycle: 30 s.

Characterization

Solution viscosity measurements were carried out in an automatic viscosimeter equipped with Ubbelohde capillaries in a mixture of phenol and 1,1,2,2-tetrachloroethane (60 : 40 by volume) at 25°C . The intrinsic viscosity, $[\eta]$, was determined by a well-known method (extrapolation using the Huggins equation). The average molecular weight, \overline{M}_w , was determined from the Mark-Houwink relation, $[\eta] = K \overline{M}_w^\alpha$. The constants were $K = 7.44 \times 10^{-4} \text{ dL g}^{-1}$ and $\alpha = 0.648$ at 25°C .¹⁷

Table II Intrinsic Viscosity $[\eta]$ and Average Molecular Weight \overline{M}_w of Modified PETV with Chain Extenders Measured at 5 Min of Residence Time

Polymer	Chain Extenders (wt %)	$[\eta]$ (dL/g)	\overline{M}_w (g/mol)	Torque Recorded at 5 Min of Residence Time (m kg)
PETV	—	0.72	40,500	2
PETV	0.9% MDI	1.01	68,200	6
PETV	0.9% HMDI	1.37	109,200	9
PETV	0.9% phenylene bis-1,4-oxazoline	0.73	41,300	2
PETV	0.9% 2,2'-bis-oxazoline	0.77	44,900	2
PETV	0.9% DGEBA	0.70	38,800	2

Infrared analysis of modified polymers was performed with a 510P Nicolet FTIR spectrophotometer from thin films prepared by compression molding at 270°C. Thirty-two scans were recorded with a 4-cm⁻¹ resolution.

Thermal analysis (crystallization temperature, T_c , melting temperature, T_m , and enthalpy of melting, ΔH_m), of the modified polymers was performed with a Perkin–Elmer DSC-4 calorimeter. The temperature used was 50–280°C with a helium atmosphere and the samples (7–10 mg) were heated at 10°C/min. The thermal stability of the modified polymers was performed with a TGA DuPont 2000 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen atmosphere.

Prior to testing the injection-molded specimens, they were conditioned at 20°C in a laboratory atmosphere for a minimum of 3 days. The reported values for all properties are the average of at least 10 determinations. Tensile tests were performed according to ISO 527, using a Zwick tensile tester Model 5101. Young's modulus measurements were made at a crosshead speed of 1 mm/min, whereas elongation measurements were made at 50 mm/min. Impact tests were performed according to Charpy ISO 179, notched specimens, using a Zwick pendulum impact tester Model 5102 (2 J).

RESULTS AND DISCUSSION

Preliminary Tests

Various types of chain extenders (Table I) were used to investigate the effect of the chain extender on the intrinsic viscosity, which is a mea-

sure of the effectiveness of the coupling reaction. Table II gives the intrinsic viscosity, $[\eta]$, the average molecular weight, \overline{M}_w , and the torque of modified PETV mechanically mixed at 64 rpm for 5 min at 270°C. The evolution of the coupling reaction is followed by the variation of the torque because this reaction induces an increase in the melt viscosity which becomes stable at the end of the reaction. The modified polymers are uncrosslinked because they are totally soluble in the mixture of phenol and 1,1,2,2-tetrachloroethane. During the processing of PETV with 0.9 wt % MDI or HMDI, we observed an increase in torque (Table II). After a residence time of 5 min, the torque becomes stable to 6 m kg for PETV with 0.9 wt % MDI and 9 m kg for PETV with 0.9 wt % HMDI. The increase and the stabilization of the torque shows that chemical reactions between the end groups of PET and the chain extenders take place very fast. The introduction of diisocyanates improves the intrinsic viscosity of PETV from 0.72 dL/g to values superior or equal to 1 dL/g and increase the molecular weight of the modified polymers (Table II). Inversely, the addition of phenylene bis-1,4-oxazoline or 2,2'-bis-oxazoline or DGEBA does not increase the torque during the processing and does not improve the intrinsic viscosity and the molecular weight of modified PETV (Table II). These results show that the diisocyanates (particularly HMDI) are more reactive toward the end groups of PET than are bis-oxazolines or diepoxide resin under the experimental conditions employed. However, branching effects contrary to crosslinking reactions are not excluded with the diisocyanates as chain extenders since modified polymers are still soluble in the mixture of phenol and 1,1,2,2-tetrachloroethane.

Table III Intrinsic Viscosity $[\eta]$ and Average Molecular Weight, \overline{M}_w , of Modified PETV with Diisocyanates Versus Residence Time

Polymer	Chain Extenders (wt %)	Properties at 2 Min of Residence Time			Properties at 5 Min of Residence Time		
		Torque (m kg)	$[\eta]$ (dL/g)	\overline{M}_w (g/mol)	Torque (m kg)	$[\eta]$ (dL/g)	\overline{M}_w (g/mol)
PETV	—	3	0.74	42,200	2	0.72	40,500
PETV	0.9% MDI	6	0.90	57,100	6	1.01	68,200
PETV	0.6% HMDI	6	0.84	51,300	—	—	—
PETV	0.9% HMDI	7	1.09	76,700	9	1.37	109,200
PETV	1.5% HMDI	9	1.70	152,300	—	—	—
PETRc	—	3	0.61	31,300	2	0.59	30,000
PETRc	0.9% HMDI	4	0.75	43,100	3	0.84	51,300

Scraps of PETRc: $[\eta] = 0.80$ dL/g and $\overline{M}_w = 47,600$ g/mol.

Subsequently to this work, we decided to study the chemical modification of virgin PET with diisocyanates.

Chemical Modification of PETV with the Diisocyanates

Effect of Mixing Time

Table III gives the torque, the intrinsic viscosity, $[\eta]$, and the average molecular weight, \overline{M}_w , of modified PETV. We observed an increase in torque of 3 m kg (at 2 min of residence time of PETV) to 6–9 m kg (at 2 min of residence time of PETV with diisocyanates) and of 2 m kg (at 5 min of residence time of PETV) to 6–9 m kg (at 5 min of residence time of PETV with diisocyanates). After 5 min of residence time, the torque becomes stable. The increase and the stabilization of the torque show that the coupling reactions take place quickly.

Equation (1)^{18,19} gives the melt viscosity versus torque recorded during the processing:

$$\eta = 4.10^4 C/V \quad (1)$$

$$\dot{\gamma} = 3.7V$$

with η (Pa s) the dynamic viscosity; C (kg/m), the torque; V (rpm), the roller speed; $\dot{\gamma}$ (s^{-1}), the shear rate. At a constant shear rate ($237 s^{-1}$) calculated by eq. (1), the melt viscosity at 270°C increases from 1800 Pa s (at 2 or 5 min of residence time of PETV) to 4000 Pa s (at 2 min of residence time of PETV with diisocyanates) to reach 6000 Pa s (at 5 min of residence time of

PETV with diisocyanates). The improvement in the melt viscosity of modified PETV with diisocyanates is a consequence of the chain-extension reactions.

The processing of PETV with 0.9 wt % HMDI or MDI during a residence time of 2 min increases the intrinsic viscosity and the molecular weight of PETV (Table III). The increase in residence time from 2 to 5 min at 270°C improves these two characteristics. These results (Table III) show that the aliphatic diisocyanate (HMDI) is more reactive than is the aromatic diisocyanate (MDI) because modified PETV with MDI at 5 min of residence time possesses the same value of intrinsic viscosity (1 dL/g) as that of modified PETV with HMDI at 2 min of residence time, which can be explained by

- The thermal stability of groups (the urethane group formed from an alcohol and an aliphatic isocyanate is more stable than is the urethane group formed from an alcohol and an aromatic isocyanate²⁰), and
- The boiling point ($T_{bp,HMDI} = 255^\circ\text{C} > T_{bp,MDI} = 200^\circ\text{C}$) of MDI, which, being lower than that of HMDI, can partially volatilize during the reaction in the batch mixer.

Thermal Properties of Modified PETV

We studied by differential scanning calorimetry (DSC) the thermal properties of modified PETV with diisocyanates (HMDI or MDI). These modified polymers are totally thermoplastic materials, fusible, and soluble in the mixture of phenol and 1,1,2,2-tetrachloroethane.

Table IV Thermal Properties of Modified PETV

	$T_{c,max}$ (°C)	$T_{m,max}$ (°C)	ΔH_m (J/g)	$[\eta]$ (dL/g)
PETV	129	248	37.6	0.72
PETV + 0.9 wt % MDI (at 5 min of residence time)	137	243	36.4	1.01
PETV + 0.9 wt % HMDI (at 2 min of residence time)	139	244	35.9	1.09
PETV + 0.9 wt % HMDI (at 5 min of residence time)	143	243	32.6	1.37

DSC thermograms of the modified samples, recorded during a second heating run at 10°C/min after quenching from the melt, show that the crystallization of modified PETV arising from the crystallization of the amorphous phase, named cold crystallization,²¹ appears at a higher temperature (Table IV), which is due to the increase in molecular weight of the modified PETV samples. T_m values show a decreasing trend with the chain extender because samples exhibit higher intrinsic viscosity. Therefore, the decreasing trend of T_m and the enthalpy of melting (Table IV) is associated with a decrease in the crystallization rate²² of the samples. The latter are expected to crystallize less effectively because of the newly created linkages which affect the crystallinity. Low T_m with increasing intrinsic viscosity is a sign of effective chain-extension reactions.

Effect of Diisocyanate Concentration

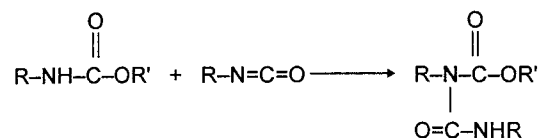
The increase in the intrinsic viscosity and the molecular weight of modified PETV with diisocyanate shows that the chain-extension reactions take place very fast (2 min of residence time). Table III gives the intrinsic viscosity and the molecular weight of modified PETV versus HMDI concentration at 2 min of residence time. The addition of 0.6 wt % HMDI improves the intrinsic viscosity of 0.74 dL/g (PETV) to 0.84 dL/g (modified PETV), which leads to an increase the molecular weight from 42,200 to 51,300 g/mol. The introduction of 0.9 or 1.5 wt % HMDI permits obtaining high values of the intrinsic viscosity ($[\eta] \geq 1$ dL/g) and molecular weight very superior to those of original PETV. We note that the addition of 1.5 wt % HMDI leads to a material possessing a very high intrinsic viscosity (1.70 dL/g) and a very high molecular weight (152,300 g/mol). There are no crosslinking reactions because this modified polymer is soluble in the mixture of phe-

nol and 1,1,2,2-tetrachloroethane. But there is very likely formation of secondary reactions in the presence of a high concentration in diisocyanate, because with the hydrogen of urethane or amide groups being labile, they can react with another isocyanate group to form allophanate or urea (Fig. 1), leading to an increase in the molecular weight of the PETV samples. We cannot quantify by infrared analysis the characteristic peaks of allophanate (1710–1750 cm^{-1}) or urea (1640–1610 cm^{-1}) because there is a large peak located at 1750 cm^{-1} on the infrared spectrum of PETV. This study shows that it is not necessary to introduce a concentration in HMDI greater than 1 wt % to improve the intrinsic viscosity and molecular weight of the PETV samples.

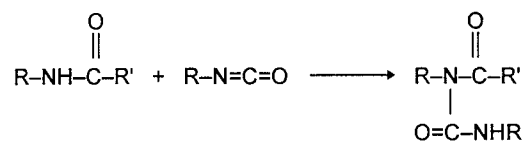
Study of Isocyanate/End Groups of PET Reaction

Gebauer et al.¹⁰ showed that the increase in molecular weight of polyesters arises only from the reactions between the hydroxyl end groups of PET and the NCO groups of the diisocyanate be-

Urethane/isocyanate reaction : allophanate



Amide/isocyanate reaction : urea

**Figure 1** Secondary reactions.

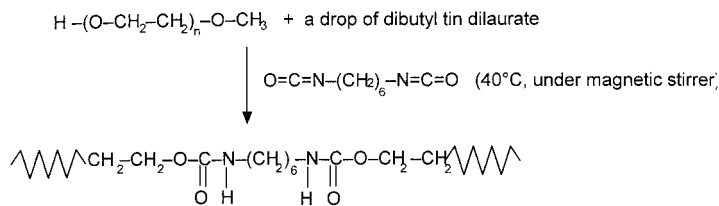


Figure 2 Model reaction.

cause of the carboxyl end group content of PET used as starting materials remains substantially unchanged. The constancy of carboxyl groups should be the result of consumption by reaction and formation by thermal degradation. Inversely, Kolouch and Michel⁹ and Akkapeddi and Ger-vasi⁷ showed that the reactions between the carboxyl end groups of PET and the NCO groups take place during the processing by reactive extrusion because there is foam formation with the release of carbon dioxide. The increase in the intrinsic viscosity and molecular weight could then be the result of coupling reactions between the end groups (hydroxyl and carboxyl) of PET and the NCO groups.

On the infrared spectrum of modified PET with 0.9 wt % HMDI, we note the absence of the characteristic peak of NCO groups situated at 2270 cm^{-1} because all NCO groups reacted with the end groups of PET. It is very difficult to locate the peaks arising from urethane groups ($1690\text{--}1740\text{ cm}^{-1}$) or amide groups (1650 cm^{-1}) because on the infrared spectrum of PETV there is a broad peak located at 1750 cm^{-1} . Consequently, we cannot quantify by infrared spectrometry the end groups of modified PET.

We studied the thermal stability of the urethane groups at the temperature of the PET processing because it is known that the addition of an alcohol

on an isocyanate is favored with regard to these of an acid on an isocyanate. To model the reaction between hydroxyl end groups and NCO groups, we reacted HMDI with PEG in the presence of dibutyl tin dilaurate (DBTDL) (Fig. 2). The kinetics of the reaction was followed by infrared spectrometry. The reaction between the alcohol and the diisocyanate is stopped when there is total disappearance of characteristic peaks of hydroxyl groups (3400 cm^{-1}) and NCO groups (2270 cm^{-1}) and the appearance of the characteristic peak of NH groups located at 3340 cm^{-1} . We studied, then, the thermal stability of urethane groups of this product by TGA. On the thermogram of PEG, we noticed a loss of weight assigned to the vaporization of light parts, with the T_d (temperature of onset decomposition) located about 170°C (Fig. 3). We note on the thermogram of urethane from PEG a loss of weight assigned to the decomposition of urethane groups, with the T_d located about 200°C (Fig. 3). Then, an isotherm was performed at 250°C for 15 min on the urethane from PEG to simulate the reaction taking place in a Rheocord Haake mixer. The thermogram shows that the urethane group is stable at 250°C for 5 min because the loss of weight is weak (inferior to 10%) (Fig. 4). So, the diisocyanates coming from the thermal decomposition of urethane groups could react with carboxyl end groups present in the middle to form amide or react with others urethane groups to

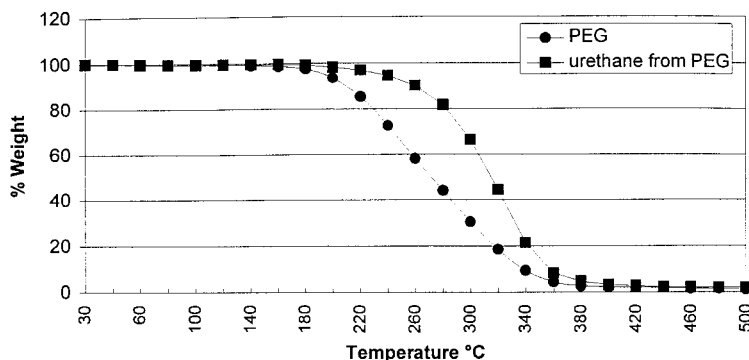


Figure 3 Thermogravimetric curves of PEG and urethane from PEG.

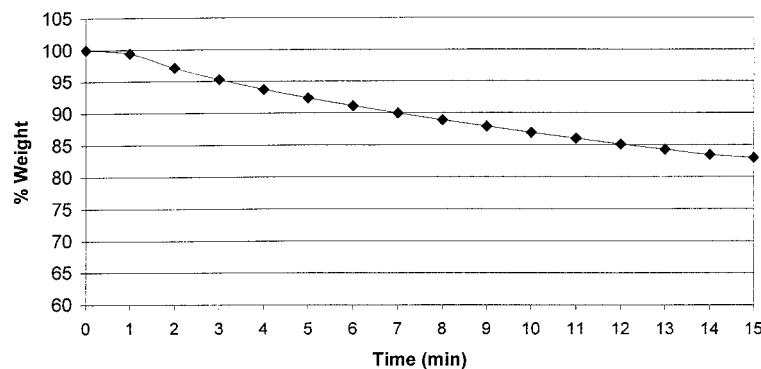


Figure 4 Isotherm at 250°C of urethane from PEG.

form allophanate. The increase in the intrinsic viscosity of modified PETV can arise from reactions between hydroxyl end groups and NCO groups (preferentially) and carboxyl end groups and NCO groups.

Chemical Modification of Recycled PET with Diisocyanate

Table III gives the torque, the intrinsic viscosity, $[\eta]$, and the average molecular weight, \bar{M}_w , of modified PETRc. Samples of PETRc with 0.9 wt % HMDI possess an intrinsic viscosity inferior to samples of PETV with 0.9 wt % HMDI (Table III) because the intrinsic viscosity of the original PETRc (0.61 dL/g) is smaller than that of PETV (0.74 dL/g), which results from the thermal history of PETRc and the specific surface of scraps which is higher than that of pellets. A high specific surface favors drying but it also favors humidity recovery before chemical treatment.⁴ So, more diisocyanate is needed when a resin with a low initial intrinsic viscosity is used. Yet, larger amounts may cause undesirable excessive crosslinking by secondary reactions of NCO with urethane groups. The results obtained with modified PETRc are very interesting because this

product possesses an intrinsic viscosity (0.84 dL/g) and a molecular weight (51,300 g/mol) at 5 min of residence time higher than those of PETV ($[\eta] = 0.72$ g/mol and $\bar{M}_w = 40,500$ g/mol).

Mechanical Properties of Modified Virgin and Recycled PET

The differences in the mechanical properties (elongation at break and impact strength) of recycled PET compared with virgin PET (Table V) can be attributed to the thermal history of the recycled material, which results in a decreased intrinsic viscosity and molecular weight.²³ Pellets of PETV or scraps of PETRc dried and the chain extender (0.9 wt % HMDI) were together injection-molded into the shape of ISO 1 test bars to study their mechanical properties. The chemical modification of PETV does not affect the Young's modulus but improves the elongation at break and the impact strength of materials (Table V). Test bars of PETV and modified PETV are transparent but a discoloration of material occurs in the presence of HMDI arising from the formation of secondary reactions. Recently, Park et al.²⁴ confirmed that NCO groups of the diisocyanates are very reactive toward the end groups of PET and that the chemical reactions take

Table V Mechanical Properties of Modified Virgin and Recycled PET

Polymer	HMDI (wt %)	Young's Modulus (N/mm ²)	Elongation at Break (%)	Charpy Impact Strength (Notched, 20°C, kJ/m ²)	Aspect of Test Bars
PETV	—	2313 (±69)	280 (±3.0)	3.0 (±0.2)	Transparent
PETV	0.9	2278 (±61)	320 (±5.0)	5.3 (±0.6)	Transparent
PETRc	—	2306 (±101)	4.6 (±0.6)	1.8 (±0.3)	Opaque
PETRc	0.9	2389 (±175)	288 (±8.0)	1.7 (±0.1)	Transparent

place very fast at 265°C.²⁵ The chemical modification of PETRc strongly improves the elongation at break from 5 to 300% (Table V). We pass then from a brittle material to a ductile material. The Young's modulus and the impact strength of modified PETRc are very close to those of PETRc. We note that the test bars of modified PETRc are transparent, whereas those made up of non-modified PETRc are opaque and that a discoloration of the material occurs in the presence of HMDI. The chemical modification of PETRc slows down the spherulitic crystallization and restores the mechanical properties enough close to those of the virgin polymer.

CONCLUSIONS

The thermal history, impurities, and shape of the particles can cause strong thermal and hydrolytic degradation of recycled PET in processing conditions. Degradative effects can be limited by using bifunctional compounds acting as chain extenders. Preliminary tests showed that the diisocyanates are more reactive toward the end groups of virgin PET than are bis-oxazolines or diepoxides under the experimental conditions used. Chemical modification of virgin PET with the diisocyanates increases the torque and the melt viscosity and leads to polymers of high molecular weight (superior to those of virgin PET) and high intrinsic viscosity (>1 dL/g). This study shows that aliphatic isocyanate is more reactive toward the end groups of a polymer than is aromatic isocyanate and that coupling reactions occur for short residence times (2 min). The improvement of molecular weight renders the material stronger toward the thermal and hydrolytic degradation and slows down the crystallization.²⁶ Modified polymers are still thermoplastic and uncrosslinked but discoloration occurs with diisocyanates. Chemical modification of recycled PET is an attractive method from an industrial point of view because it allows an increase of the intrinsic viscosity of a recycled polymer in one-step processing. This method leads to a material having an intrinsic viscosity, molecular weight, and mechanical properties close to those of virgin PET.

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