

# Characterization of Recycled/ Virgin PET Polymers and their Composites

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**Abstract:** In this investigation two Poly (Ethylene Terephthalate) (PET) polymers obtained from mineral water bottle and a virgin PET polymer were characterised by viscosimetry, differential scanning calorimetry (DSC) and rheology. Virgin PET showed better rheological and viscosimetric properties compared to recycled PET polymers. In order to improve properties when reprocessed at high temperatures, recycled polymers were blended with the virgin one. Rheological and thermal properties of extruded recycled/virgin (PET-V/R) composites showed a good rheological and thermal compatibility and stability compared to extruded pure recycled polymers.

**Keywords:** PET, Recycled, Composites, Rheology and Polymer

## 1. Introduction

A major problem faced by the plastics industry is that of waste disposal. Recycling material would appear to offer a solution which is satisfactory in terms of preventing environmental pollution. Increasing interest has recently, been focused on the recycling of plastic wastes, especially PET (1). The former is already being recycled and a number of uses have been found for it, including: fibrefill, fabric, automotive parts, industrial strapping, sheet and film, new containers for both food and non-food products, containers for baked goods. From this wide variety of regenerated materials, numerous applications for recycled polyesters can be explored depending on the properties of the resin.

Recycling of PET can be carried out according to different strategies. In particular, the post-consumer PET can be depolymerised to re-use the regenerated monomers as raw materials for a new polymerisation process (chemical recycling) or can be reprocessed after washing and milling (mechanical recycling). Otherwise, a common problem faced during mechanical recycling of PET is the degradation of the polymer that leads to the reduction of its average molecular weight  $M_w$  (2), as well as to mechanical properties deterioration (3). In fact, during processing, PET undergoes three different degradation phenomena, namely thermal, mechanical and hydrolytic chain scission. According to Regel

and Michaeli (4), hydrolytic chain scission is the fastest and the most dangerous degradation process. Thermal exposure, as well as shear degradation with the simultaneous presence of retained moisture and physical contaminants (PE, PVC, adhesives...), will also lead to a remarkable  $M_w$  loss during reprocessing at high temperatures. These losses will result in plastic material with reduced rheological and mechanical properties. Many solutions were proposed in literature, Torres (5), Cardi (6), Rosu (7), Incarnato (8), to overcome this problem. Among these, we mention the intensive cleaning and drying of PET flakes before extrusion, the sorting of impurities and the use of chain extenders or modifiers.

Using recycled polymer in blend with virgin polymer of the same nature is a common solution for upgrading post-consumer materials. Scarfato and La Mantia (9), has studied composites of recycled PA6 and virgin PA. They found that the composites prepared in specific conditions show rheological and mechanical properties close to those of the virgin polymer. Kukaleva et al. (10), investigated composites of recycled and virgin HDPE polymers. They stated that mechanical properties (modulus and elongation) of the composites have predictable linear behaviour.

Earlier Wenguan (11), prepared and characterised homopolymer composites of recycled/virgin PVC. He found that the properties of the composites are between those of the pure compounds.

The aim of this work is using composites of recycled PET and virgin PET to maintain the properties of the recycled polymer sufficiently high during the transformation processes.

## 2. Experimental

### 2.1. Materials

Three types of materials were investigated in this study: two PET bottle waste polymers and a virgin one. Chips of

**Table I.** Intrinsic Viscosity, molecular weight and MFI of the three PET polymers

	$[\eta]$ (dL/g)	$M_w$ (g/mol)	$M_n$ (g/mol)	MWD ( $M_w/M_n$ )	MFI (g/10')
PET-A	0,67	35500	17700	2,03	26
PET-B	0,63	32300	16100	2,01	30
PET-C	0,74	42100	20200	2,1	20

### 2.2. Melt Processing

It should be pointed out that PET chips or flakes have to be dried before extrusion; otherwise the molecular weight will be considerably reduced. The moisture content of PET should not exceed 0.005%. So, recycled chips and virgin pellets were dried under vacuum during 12H at 90 °C in order to eliminate the residual moisture. Then, composites of virgin/recycled PET (PETV/R) were obtained using a Haake-Rheocard twin screw extruder under the following conditions: die temperature 270 °C, extrusion speed 40 rpm and residence time of 5mn. The extrudate is cooled in water then passed through a pelletizing unit. We considered the following compositions of composites: 90/10, 70/30, 50/50 and 25/75 (PETV/ PETR w/w).

### 2.3. Methods of Analysis

Solution viscosity measurements were carried out on a Scött Gerate viscosimeter equipped with Ubbelohde capillary in a solution of phenol and 1,1,2,2-tetrachloroethane (60 / 40 w/w %) at 25 °C. the intrinsic viscosity,  $[\eta]$ , of polymers was extrapolated using the Huggins equation. The average molecular weights,  $M_w$  and  $M_n$ , were then computed from the values of  $[\eta]$  according to the following relations, Berkowitz (12) and Kokkalas (13):

$$\bar{M}_w = 6,58.10^4 [\eta]^{1,54} \quad (\text{Eq. 1})$$

$$\bar{M}_n = 3,29.10^4 [\eta]^{1,54} \quad (\text{Eq. 2})$$

The Melt Flow Index (MFI) which is a local measurement of melt viscosity were measured using a MFI-MVI 3350 apparatus according to the norm ISO 1133 (275 °C /2,16 kg / 2,1 mm).

A TA Instruments calorimeter was used to obtain thermograms of virgin, recycled and blended PET polymers.

The swept temperature lies between 30 and 280 °C under nitrogen atmosphere and an empty capsule as reference. The calorimeter is attached to a thermal analysis data station that

crushed and cleaned bottles, purchased from an industrial plastic waste collector, were used as the source for recovered PET materials. Recycled PET (PET-A) comes from blue post-consumer bottles and recycled PET (PET-B) arises from heterogeneous deposits of various coloured bottles (white, green ...etc). A fiber grade PET (PET-C) was used as the virgin PET resin. The characteristics of these three starting polymers are recapitulated in table I.

calculates glass transition temperature,  $T_g$ , crystallisation temperature,  $T_c$ , melting temperature,  $T_m$ , enthalpy of crystallisation,  $\Delta H_c$ , enthalpy of melting,  $\Delta H_m$  of samples. The percent of crystallinity,  $\chi_c$ , for all PET samples was calculated from Eq. 3 whenever a crystallisation exotherm was present during heating:

$$\chi_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} * 100 \quad (\text{Eq. 3})$$

Where  $\Delta H_m^0 = 32,5 \text{ cal/g}$ , is the heat of fusion of a 100 % crystalline PET (14).

Dynamic and steady shear rheological measurements were carried out on a dynamic rheometer MCR500 from Physica. This operates at both controlled stress and strain modes. The rheological properties of molten materials were determined using parallel plate geometry: 25 mm diameter and a constant gap of 1 mm. Steady shear viscosity measurements were carried out in a shear rate range varying from 0,1 to 300  $\text{s}^{-1}$ . For very higher shear rates the data obtained were inconsistent due to the fact that molten polymer ejected outside of measurement gap because of the important centrifuge force that develops at high rotation speed of superior plate.

For dynamic tests, the strain ( $\gamma$ ) values are chosen in order to perform the frequency sweeps in the linear viscoelastic range (LVR) i.e., the limiting strain under which the rheological parameters ( $\eta^*$ ,  $G'$ ,  $G''$ ...) remained constant. For this purpose, preliminary strain sweeps were made, at constant frequency (1 Hz) and temperature (270 °C), and the LVR was determined for each polymer. The frequency range investigated was 0,1-100 Hz with a constant shear strain of 10 % (within the LVR of polymers).

## 3. Results and Discussion

### 3.1. Thermal and Rheological Properties of as Received Recycled and Virgin PET Polymers

#### 3.1.1. Differential Scanning Calorimetry (DSC) Analysis

DSC Measurements were carried out on as received virgin

and recycled PET polymers. A heating run was performed from 30 to 280 °C at a rate of 10°/mn.

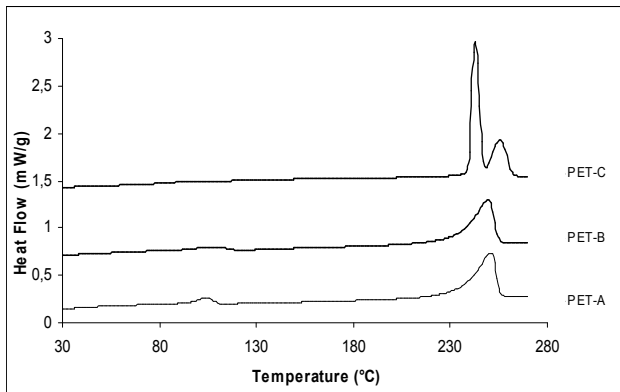


Fig. 1. DSC thermograms of PETs during heating.

On figure 1, we note that the thermogram of the virgin PET (PET-C) exhibits two melt peaks. The existence of these two peaks is due to the reorganisation of the crystals during the heating run on DSC (15). During DSC heating run, a reorganisation process of crystalline fraction takes place. The first endotherm (at 243 °C) is due to the melting of small imperfect crystals formed at a constant crystallisation temperature; the second endothermic peak (at 252 °C) represents the fusion of originally more perfect crystals that have suffered a reorganisation during the scan in such a way that they melt at higher temperatures. Unlike virgin PET, the recycled PET polymers exhibit only one melt peak. This can perhaps be explained in terms of orientation. The recycled PET (coming from soft drink bottles) possesses a bi-axial crystalline orientation along which the polymer chains are fixed and thus cannot be reorganised during the temperature scan.

Also the pellets of virgin PET exhibit 49 % crytallinity, whereas the recycled PET scraps presents only 34 % crytallinity for PETA and 33 % for PETB. Note that the value of crytallinity rate for virgin PET is calculated according to the higher peak that represents the sample state before scan.

### 3.1.2. Rheological Properties

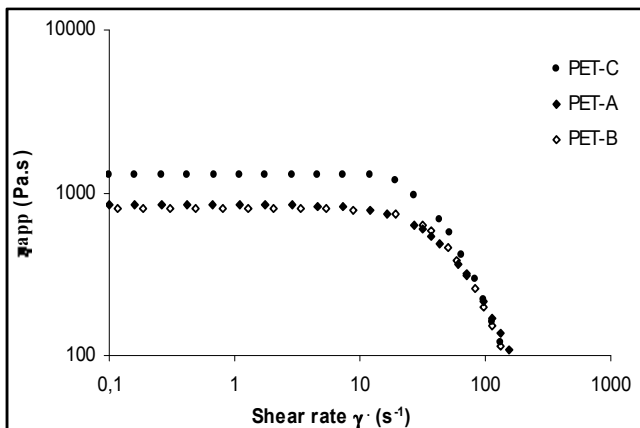


Fig. 2. Flow curves at 260 °C of recycled and virgin PET polymers.

Flow curves at shear rates ranging between 0,1-300 s<sup>-1</sup> of the PET polymers are shown in figure 2.

It can be seen that virgin PET have higher apparent shear viscosity than recycled polymers. This difference is mainly noticeable at the Newtonian region (characterised by zero shear viscosity  $\eta_0$ ). The higher melt viscosity of PETC is explained by its higher macromolecular weight Mw and weak fluidity (MFI).

The variation of storage modulus G' and loss modulus G'' as a function of frequency is reported on figure 3. It is seen that PETC has higher loss and storage modulus values than those of PETA and PETB. That is virgin PET has a stronger viscoelasticity than recycled PET polymers. It appears also that for all the three PET materials analysed the loss modulus G'' is higher than the storage modulus G' in the whole frequency range investigated. This indicates that the viscous flow of the materials dominates the elastic character in the temperature and the frequency range investigated.

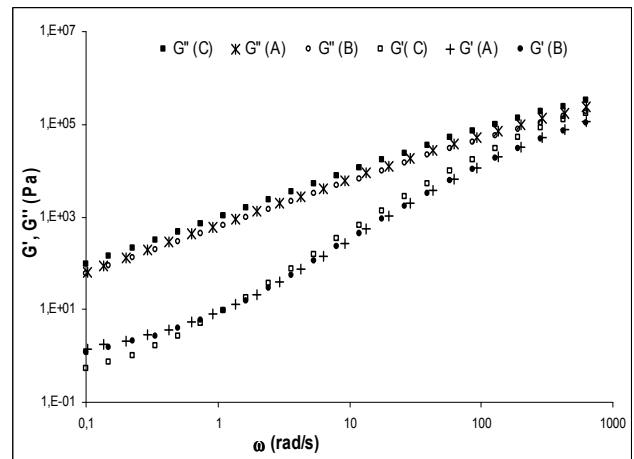


Fig. 3. G' and G'' in conjunction with  $\omega$  for PET polymers.

### 3.2. Thermal and Rheological Properties of PET-V/R Composites

#### 3.2.1. Thermal Analysis

DSC analysis of PET-V/R blend pellets was carried out following this experimental protocol:

- a heating step from 20 to 280 °C at a rate of 10°/mn
- a thermal treatment at 280 °C for 3 minutes
- a crystallisation step from 280 °C down to 20 °C at 10 °C/mn.

The thermograms recorded during the heating run of PET-C/A composites are reported on figure 4. The same behaviour is also observed for PET-C/B composites.

The PETV/R thermograms show:

- a glass transition temperature (Tg) that remains almost constant for all the PET-V/R composites ( 83-84 °C ) .

- an exothermic peak known as “cold crystallisation” (16), corresponding to the crystallisation of amorphous phase. This peak is typical for semicrystalline polymers such as PET or PEEK The phenomenon of cold crystallisation is explainable. As the frozen chains are heated, a critical mobility for crystallisation is reached and the material organises with an

exothermic process. From the table II, we observe that the values of the cold crystallisation temperature ( $T_{cc, min}$ ) of our composites increase with increasing recycled PET content.

- an endothermic peak associated with the fusion of the whole crystalline structure. We can see on figure 4 that the values of melting temperatures ( $T_{m, max}$ ), that corresponds to the maximum of the melting peak, of the PET-V/R composites decrease with the PETR concentration and are between those of the starting materials i.e. PETR and PETV. This absence of melting depression or synergy was explained by Fann *et al.* (17) by the fact that PET/PET composites are crystalline-crystalline isomorphous polymer composites of the same material (PET).

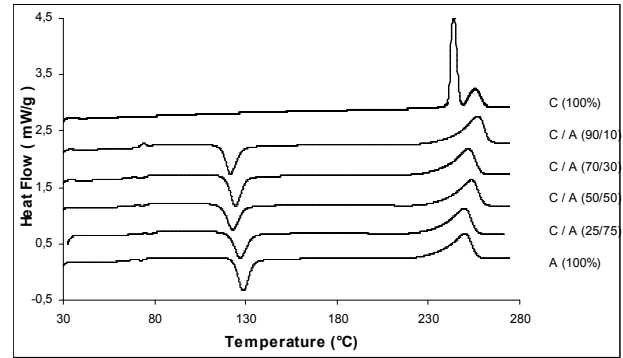


Fig. 4. Thermal behaviour during heating run of PET-C/A composites.

Table II. Thermal Analysis (DSC) of the PET-V/R composites.

	$T_g$	$T_{m, max}$	$\Delta H_m$ (J/g)	$T_{cc, min}$	$\Delta H_{cc}$ (J/g)	$\chi$ (%)	$T_{c, min}$	$\Delta H_c$ (J/g)
PET-C (100%)	83	255	55,8	-	0	41	199	36
PET-C/A (90/10)	83	257	39,5	121	26,1	10	211	44,6
PET-C/B (90/10)	83	257,5	38,7	119	23	11,5	212	44
PET-C/A (70/30)	84	255	38,1	124	27,1	8	213	42,9
PET-C/B (70/30)	84	254,5	35,7	122	21,2	10,6	213,5	45,1
PET-C/A (50/50)	84	253,5	40,6	125	25,5	11	213	44,3
PET-C/B (50/50)	84	253	38,2	124	22,1	12	214,5	43,9
PET-C/A (25/75)	84	252	37,5	129	23,8	10	212	43,6
PET-C/B (25/75)	84	255	44,5	127	20,7	17,5	217,5	44,1
PET-A (100%)	85	251	45,5	131	21	18	217	38,6
PET-B (100%)	85	254	44,3	129	22	16	218	37,8

DSC curves obtained from the cooling run of PET-V/R samples are plotted on figure 5.

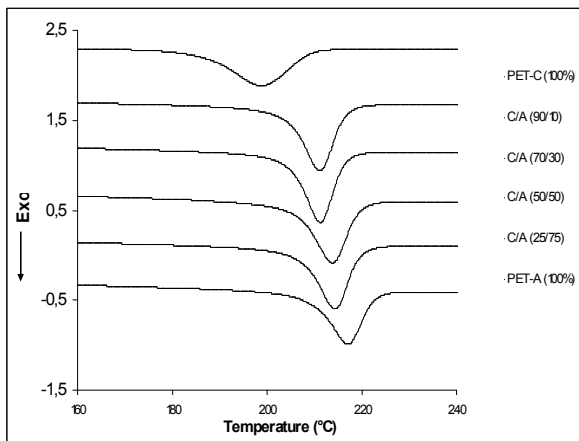


Fig. 5. Thermal behaviour during crystallisation run of PET-C/B composites.

Contrary to other samples, PETC exhibits a rather broad temperature range of crystallisation starting at a lower temperature than other materials. However, recycled PET polymers (PETA and PETB) show higher crystallisation temperatures  $T_c$  ( $\sim +20$  °C) with a sharper and narrower temperature range of crystallisation than PETV. This is explainable by the lower molecular weight (Mw) of PETR polymers and the physical contaminations that they may contain that will act as nucleation agents for crystallisation kinetics.

On the other hand, PET-V/R composites show various degrees of improvement on the crystallisation process. Their

crystallisation is more narrow and sharper than parent polymers. We can also depict from table V that minimum crystallisation temperature ( $T_{c, min}$ ) of the composites increase with the increase of PETR composition.

### 3.2.2. Rheological Behaviour of PET-V/R Composites

Steady state rheological properties of virgin/recycled PET composites were determined at shear rates ranging between  $0,1-300$   $s^{-1}$  at constant temperature  $260$  °C. The flow curves obtained for different composites are reported on figure 6.

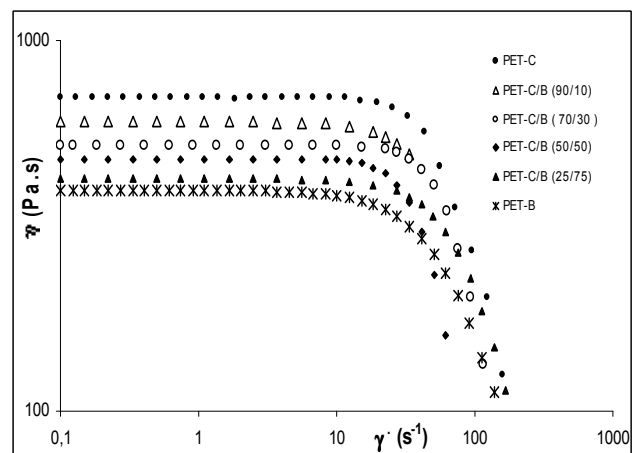


Fig. 6.  $\eta_{app}$  vs  $\dot{\gamma}$  for PET-C/B composites (at  $260$  °C).

We remark that the apparent viscosity increases with the increase of PETR percentage for the two types of composites PET-C/A and PET-C/B. Also the viscosities of all the composites lie between those of pure PET materials.

Furthermore, it can be noted that the viscosity of the composites PET-C/B is higher than that of the composites PET-C/A. This is probably due to the fact that the PET-A is more likely to degrade than the PET-B. Indeed, during the preparation of the composites the polymers undergo shearing, thermal and mechanical stress (temperature and pressure).

The zero shear viscosity of the PET-C/A composites is plotted in conjunction with the PETV weight fraction (figure 7).

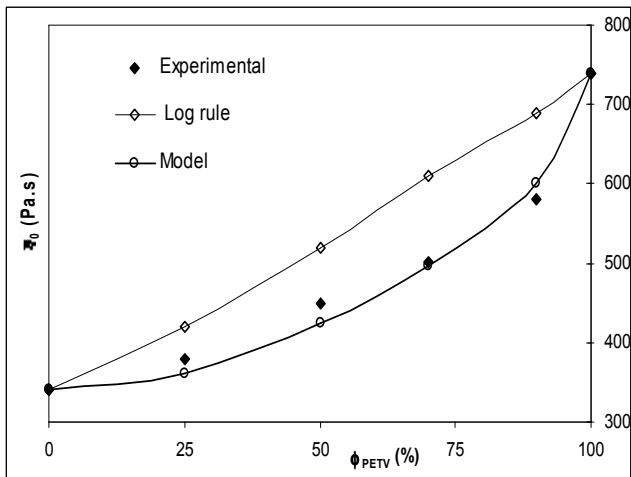


Fig. 7. Negative deviation of  $\eta_0$  in conjunction with composition for PETC/A composites.

The experimental curves show a negative deviation (ND) from the logarithmic additivity rule frequently used to model polymer/polymer composites viscosity [18]. The logarithmic rule is written as:

$$\ln \eta_m = \sum_i \phi_i \ln \eta_i \quad (\text{Eq. 4})$$

where:  $\eta_m$  : viscosity of the blend;  $\phi_i$  : weight fraction of constituent  $i$  ( $i = 1, 2$ ) and  $\eta_i$  : viscosity of component  $i$ .

Dynamic rheological properties ( $\eta^*$ ,  $G' = \eta''/\omega$  and  $G'' = \eta'/\omega$ ) for the PETV/R composites and extruded pure polymers (PETR and PETV) were measured with constant strain of 10% at 260 °C.

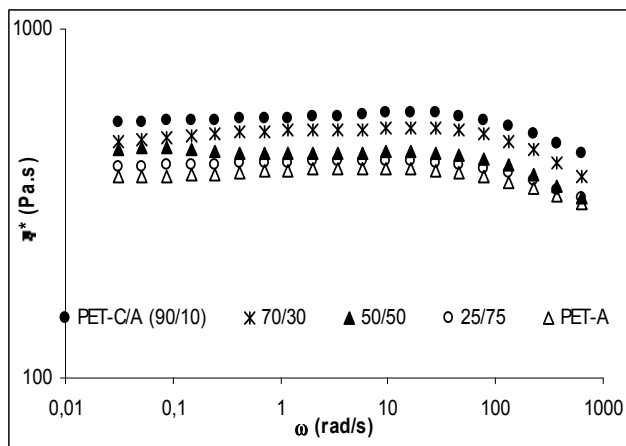


Fig. 8.  $\eta^*$  of PET-C/A composites at 260 °C.

As expected the dynamic viscosity ( $\eta^*$ ) decreases with frequency (figures 8). Also, as for steady state shear viscosity, the complex melt viscosity increases with virgin PET concentration.

In order to analyse the dynamic rheological data, the Cole-Cole plot ( $G'$  in conjunction with  $G''$ ) was used. This criterion was developed by Han and Kim (19). In this method, if a blend is miscible the same slope is observed between the blend compositions and pure components; otherwise it is considered to be immiscible or phase separated blend. On figure 9, the plots showed almost the same slope for all the PET-V/R composites which is a good criterion proving the miscibility of recycled and virgin PET polymers. The independence of composition and the absence of phase separation would mean that PETV and PETR are miscible down to the macromolecular level. The PET-V/R composites would so form an isotropic medium that has no separate domains occupied by the respective constituent components.

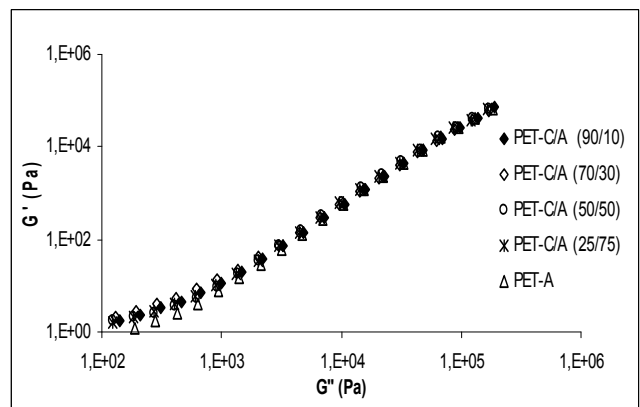


Fig. 9. Cole-Cole analysis of viscoelastic modulus of PET-C/A composites.

## 4. Conclusions

Structural and molecular characterization of virgin and recycled PET polymers has showed differences between these two types of polymers. Virgin PET has higher macromolecular weights (and therefore higher viscosity) and lower melt flow index (MFI) than recycled PET polymers. This is mainly due to degradation of recycled PET that undergone temperature and shear during previous processing operations (bottle manufacturing).

The study of thermal behaviour of composites of virgin/recycled PET points out the good microstructural morphology of the composites. The absence of melting depression or synergy was explained by the fact that PETR/PETV composites are crystalline-crystalline isomorphous polymer composites of the same material. This statement was in accordance with rheological measurements. The steady and dynamic tests showed the absence of phase separation that would mean that PETV and PETR are miscible down to the macromolecular level. The PET-V/R composites can be considered as forming an isotropic medium that having no separate fields occupied by the respective constituent components.

Thus, the study reveals that the mechanical blending of recycled PET chips and virgin PET pellets improves the melt processing of recycled PET.

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