

¹³C Solid State Characterization of Recycled Poly(ethylene terephthalate)-(PET)**C. R. Nascimento, M. L. Dias**Instituto de Macromoleculas Professora Eloisa Mano - Universidade Federal do Rio de Janeiro P.O.
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Abstract: *The improvement of recycled poly(ethylene terephthalate) (PET) properties has been an object of great economical importance mainly because PET applications have increased in the last decade. However, recycled PET can contain residual contaminants from the recycling process that can reduce its properties and applications. In order to improve the recycled PET applications, crystallization under certain annealing conditions and a solid state polymerization reaction are normally carried out. The annealing process and molecular dynamics of a recycled PET were investigated by ¹³C high-resolution solid-state NMR and differential scanning calorimetry (DSC). An increase in the PET crystallinity was observed by DSC method employed with the annealing conditions. Changes in the PET ¹³C CP/MAS NMR lines shape and ¹H spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$) correlate linearly with PET crystallinity.*

The application of post-consumer plastics for several products as raw material has increased in the last decade. However, recycled plastics are still used in low value products or mixed with virgin resin to supply material specification. In most of the cases, recycled plastics can be considered inferior due to the presence of residual contaminants or changes in molecular structure caused by degradation during the recycling process. However, their properties can be improved by a solid state polymerization reaction that normally takes place below the crystalline melting temperature (T_m) under nitrogen flow.

High-resolution solid-state NMR is a powerful tool to study polymer dynamics and chemical structure. In this study we investigated the influence of annealing time and annealing temperature in PET molecular

motion by ¹³C solid-state NMR and thermal properties measurements.

The recycled PET (sample A) was crystallized for 4h (sample B) and 16 h (sample C) at 150°C. Sample D was crystallized at 150°C for 16h and reacted for 16h at 230°C. Sample E was crystallized for 16h at 170°C.

The thermal behavior of the samples, T_m and ΔH , was determined using a Perkin Elmer, model DSC 7, differential scanning calorimeter under nitrogen atmosphere. The heating run was performed at 10°C/min and the range of temperature was varied from 25 to 300°C. The crystallinity degree (X_c) was calculated by the equation:

$$X_c = \Delta H_m / \Delta H^0 \times 100,$$

where $\Delta H^\circ = 32.5 \text{ cal/g}$ (1) and ΔH_m is the total melting enthalpy in the run.

Samples A, B, C, D and E were examined using ^{13}C solid-state NMR with cross polarization (CP) and magic angle spinning (MAS). These tests were conducted at room temperature using a Varian INOVA-300 (7.1T) NMR spectrometer operating at 75.4 MHz for ^{13}C . A pulse width of 90° ($4.5 \mu\text{s}$) was applied with a recycle delay of 3s and 512 transients were accumulated. A spectral width of 50 kHz and an acquisition time of 0.05s were used for data collection. The contact time was $1500 \mu\text{s}$. The spectra were referenced to the hexamethylbenzene (methyl peak at 17.3 ppm from TMS). The power of pulses were calibrated to achieve Hartmann-Hahn conditions. The samples were spun at 4.0 kHz of MAS in 7mm zirconia rotor. ^1H relaxation times in the rotating frame ($T_{1\rho^H}$) were measured using a standard procedure based

on a variable spin-lock period preceding a constant cross-polarization time. Twelve points were acquired in the range of $200 \mu\text{s}$ to 12 ms.

Table 1 shows that the T_m of the samples and the activation energy (ΔH_m) increase with increasing the annealing time and temperature, except for samples A and B. It is an indication that the crystals form are probably being modified by the thermal treatment. The $T_{1\rho^H}$ values measured for the methylene carbon of PET samples at 62ppm increase gradually from sample A (5.1ms) to sample E (8.7ms), which indicates that molecular motion is reduced with more severe annealing conditions. Figure 1 shows the ^{13}C CPMAS NMR spectra of annealed PET samples (from sample A to sample D). The lines at 63, 134 and 164 ppm correspond to methylene, phenyl and carbonyl-carbon of PET main chain, respectively.

Table 1. Thermal properties, crystallinity and $T_{1\rho^H}$ of PET samples.

PROPERTIES	SAMPLES				
	A	B	C	D	E
T_m' ($^\circ\text{C}$)	-	165.9	168	-	199
T_m ($^\circ\text{C}$)	247	242.1	246	269	249
$\Delta H_m'$ (J/g)	-	2.0	4.5	-	3.5
ΔH_m (J/g)	40.8	38.6	43.8	61.5	49.5
X_C (%)	30.0	28.4	32.2	45.2	36.4
X_{CT} (%)	-	29.9	35.5	-	39.0
$T_{1\rho^H}$ (ms) at 62ppm	5.1	7.8	8.2	8.4	8.7

(A) untreated recycled PET; (B) annealed at $150^\circ\text{C}/4\text{h}$;
 (C) annealed at $150^\circ\text{C}/16\text{h}$; (D) annealed at 150°C /reacted for $230^\circ\text{C}/16\text{h}$;
 (E) annealed at $170^\circ\text{C}/16\text{h}$
 T_m and T_m' are the T_m of main and secondary peaks,
 ΔH_m and $\Delta H_m'$ are the melting enthalpies of main and secondary peaks,
 X_C is degree of crystallinity, using the contribution of the main peak ;
 X_{CT} is degree of crystallinity, using the main peak and secondary peak ;

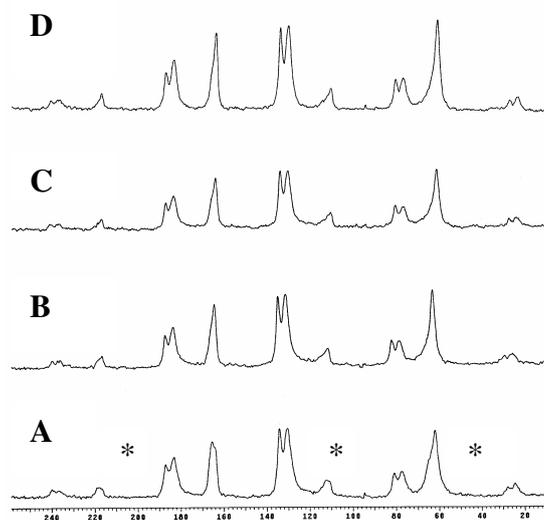


Figure 1. ^{13}C CPMAS spectra of PET samples (* spinning side bands)

The methylene carbon (63ppm) for sample A (the least crystalline sample) becomes narrower as the annealing time and temperature increases (from spectrum A to D). This is an indication that the crystallization degree is increasing as the annealing time and temperature also increases. NMR data

corroborate well with thermal properties and crystalline measurements and help to follow molecular motion changes during the annealing process of PET samples.

References

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