

Improved Dispersion of Clay Platelets in Poly(butylene terephthalate) Nanocomposite by Ring-Opening Polymerization of Cyclic Oligomers: Effect of the Processing Conditions and Comparison with Nanocomposites Obtained by Melt Intercalation

C. Berti,¹ E. Binassi,¹ M. Colonna,¹ M. Fiorini,¹ T. Zuccheri,¹ S. Karanam,² D. J. Brunelle³

¹Dipartimento di Chimica Applicata e Scienza dei Materiali, Università degli Studi di Bologna, Viale Risorgimento 2, 40122 Bologna, Italy

²SABIC Innovative Plastics, Laan, Bergen Op Zoom, Netherlands

³General Electric, Global Research Center, One Research Circle, Niskayuna, New York 12309

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ABSTRACT: Poly(butylene terephthalate) nanocomposites with organically modified montmorillonites have been prepared by *in-situ* ring opening polymerization of PBT cyclic oligomers. High molecular weight polymers can be obtained by choosing the proper polymerization conditions and catalyst in very short polymerization time (10 min) and low temperature (205°C). A better dispersion of the clay and a consistently higher M_w

have been obtained by this method respect to the standard melt intercalation approach, leading to improved thermo-mechanical properties of the nanocomposite. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3211–3217, 2009

Key words: clay; nanocomposite; polyesters; ring-opening polymerization

INTRODUCTION

Nanocomposites are a class of composites for which at least one of the dimensions of the dispersed phase is in the nanometer range and often present superior physical and mechanical properties over their microcomposites counterparts, including improved modulus, reduced gas permeability, flame retardancy, and improved scratch resistance.^{1–7} Much of the work in this area has been focused on polymeric nanocomposites derived from layered silicates such as montmorillonite clay (MMT).

The three methods reported in the literature^{1,2} for the preparation of the polymer/clay nanocomposites are:

- Melt intercalation—consists of the mixing of the molten polymer with the layered silicate.
- *In-situ* intercalative polymerization—consists of the swelling of the layered silicate with the liquid monomer and the subsequent polymerization.

- Exfoliation adsorption—consists of the exfoliation of the silicate layers using a suitable solvent and adsorbing the polymer onto the delaminated sheets and eventually the solvent evaporated.

The melt intercalation process is one of the most studied since permits the straightforward preparation of nanocomposites by melt extrusion of the polymer with the silicate.^{1,2}

To obtain an exfoliated nanostructure, it is necessary to modify the sodium MMT by exchanging the sodium ions with amino acid salts or quaternary ammonium salts bearing long alkyl chains.^{1,5} The low-thermal stability of the ammonium salts commonly used for the modification of the clay is one of the main issues connected with the preparation of some semicrystalline polymers (e.g., terephthalate polyesters) nanocomposites since the temperature of the melt intercalation and of the *in-situ* polymerization processes is very close or sometimes above the degradation temperature of the ammonium salts.

Polymer nanocomposites comprised of a semicrystalline polymer matrix are particularly attractive due to the dramatic improvement in heat distortion temperature (HDT) and modulus provided by the nanoparticle reinforcement. Polymer/clay nanocomposites of most commodity semicrystalline thermoplastics such as nylon-6,^{3,4,8} poly(ethylene terephthalate)^{9–14} (PET) and poly(butylene terephthalate)^{15–26} (PBT) have

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Correspondence to: M. Colonna (martino.colonna@unibo.it).

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been studied in detail. Several articles and patents reports the preparation of nanocomposites of poly(alkylene terephthalate).^{9–26} However, no complete exfoliation of the clays has been reported for standard poly(alkylene terephthalate)s nanocomposites using the melt intercalation or the *in-situ* polymerization approaches. On the contrary, a higher degree of exfoliation has been reported for PET^{27,28} and PBT^{29–32} using the *in-situ* ring-opening polymerization (ROP) of cyclic oligomers. Indeed, cyclic oligomers present a consistently lower melt viscosity respect to linear polymers and therefore are able to intercalate inside the galleries of the organically modified clays.^{33–38} Moreover, the polymerization of the cyclic oligomers is very fast and high-molecular weight polymers can be obtained in very short times.³¹ The rapid polymerization of the cyclic oligomers causes an increase of the interlayer distance along with the disintegration of the layered silicates. In addition, the high-reaction temperature required for the melt intercalation method gives rise to consistent thermal degradation and M_w drop of the polymer matrix (in particular for quaternary ammonium surfactants), whereas the ROP can be successfully performed at temperatures below 210°C at which the polymer matrix and the clay are stable.

The methods reported in the literature^{26–30} for the use of cyclic oligomers comprise a step involving the dissolution of the cyclic oligomers in a solvent followed by the mixing with the MMT for several hours and by the evaporation of the solvent, making this method unsuitable for industrial applications. Moreover, very low-molecular weight polymers have been generally reported,^{26–29} mainly due to the low purity of the oligomers used and to a not well-optimized polymerization procedure. Very high temperature (even exceeding the melting temperature of PBT) has been used in most of the articles^{26–29} regarding the synthesis of terephthalate polyester nanocomposites by *in-situ* ROP of cyclic oligomers. To the best of our knowledge there are no articles in the literature that reports a method for the preparation of PBT nanocomposites by *in-situ* ROP of cyclic oligomers without the use of a solvent to mix the clay with the cyclic oligomers. Moreover, no data regarding the thermomechanical properties of the composite are present in the literature

Therefore, we have studied the preparation of PBT nanocomposites by ROP of cyclic oligomers the presence of an organically modified MMT putting the attention on the process conditions and on the purification procedure of the oligomers. We also report the thermomechanical properties of the nanocomposites and a comparison with nanocomposites obtained by the classic melt-intercalation technique on commercial PBT.

EXPERIMENTAL

Reagents

General Electric PBT VALOX195 (M_w 54,100, M_n 26,300) was a gift of General Electric Plastics. Dibutyltin oxide, trimethyl-orthoacetate, diazabicyclo[2.2.2]octane (DABCO), triethylamine, terephthaloyl chloride, 1,4-butanediol, and ethylene glycol (all from Aldrich Chemicals) were high purity products and not purified before use.

Dellite MMT clays from Laviosa Chimica Mineraria (Italy) were dried overnight at 100°C before use. The two clays used were the pristine sodium MMT (Dellite HPS, d -spacing = 12.9 Å, CEC = 128, particle size = 6–8 μm, loss on ignition = 6–8%) and a MMT exchanged with an ammonium salt bearing two hydrogenated tallow chains and two methyl groups (Dellite 72T, d -spacing = 25.2 Å, CEC = 128, particle size = 6–8 μm, loss on ignition = 36–38%).

Preparation of cyclic dibutyltin initiator (1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane)

Dibutyltin oxide (29.9 g, 0.12 mol) and ethylene glycol (7.54 g, 6.67 mL, 0.12 mol) were charged into a 500 mL flask containing distilled toluene (63 mL). The flask is fitted with a sidetrapp condenser system to collect distillate and return overflow to the reaction vessel. The reagents were slowly heated to reflux until the dibutyltin oxide dissolved. The reaction was stopped when the water level in the trap appears to be constant. The crude reaction product was dried under dynamic vacuum for 24 h at 50°C.

1,4-Butylene terephthalate cyclic oligomers synthesis³¹

A three-neck 5-L flask was fitted with a mechanical stirrer, nitrogen purge, and a pair of calibrated peristaltic pumps for controlled addition of reagents. The reactor was charged with 3 L of dry CH_2Cl_2 (<20 ppm water), 1.7 mol of triethylamine (235 mL), and 40 mmol of DABCO (4.48 g). A 1.0M solution of terephthaloyl chloride in CH_2Cl_2 (800 mL) and neat 1,4-butanediol (72 g; 0.80 mol) were added at a constant rate over 30 min to 1 h, using the peristaltic pumps to maintain stoichiometry in the reactor. The reaction was mildly exothermic, reaching reflux temperature in about 20 min. Five minutes after the reaction was complete a small sample was quenched with water, washed with HCl, filtered, and analyzed by HPLC. If hydroxybutyl linear oligomers were detected, a small portion of TPC was added to the reactor to convert them to acid chloride-terminated oligomers. When linears were no longer detected, the reaction was quenched with a small amount of water (10 mL), followed by addition of aqueous

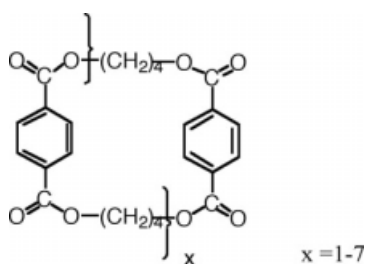


Figure 1 PBT cyclic oligomers.

NH_4OH (10 mL). Polymer was removed by filtration through Celite, and the CH_2Cl_2 solution was worked up by washing sequentially with 3N HCl, 1N HCl, and water (three times). Filtration and evaporation provided the crude PBT cyclics (Fig. 1) in 82% yield.

Cyclic oligomers purification and polymerization

The polymerization of cyclic oligomers have been conducted on the cyclic oligomers dried overnight at 105°C and after purification using trimethyl-orthoacetate as capping agent with the procedure previously reported in the literature³¹ using 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxy-acyclodecane as catalyst (0.3 mol %). After the addition of the clay and capping agent, the oligomers were stirred for 15 min and for additional 3 min under dynamic vacuum to remove by-products formed during the capping reaction and then for 1 h under nitrogen.

After the catalyst addition, the polymerization is very fast and within 15 s the molten cyclic oligomers become too viscous to be mechanically stirred. Crystallization of the polymer usually occurs within 5 min and the reaction mixture was kept reacting in the solid state for additional 5 min. We have found that 205°C is the optimal reaction temperature since the unreacted cyclic oligomers level is below 2% (as detected by $^1\text{H-NMR}$) and the polydispersity is 2.2.

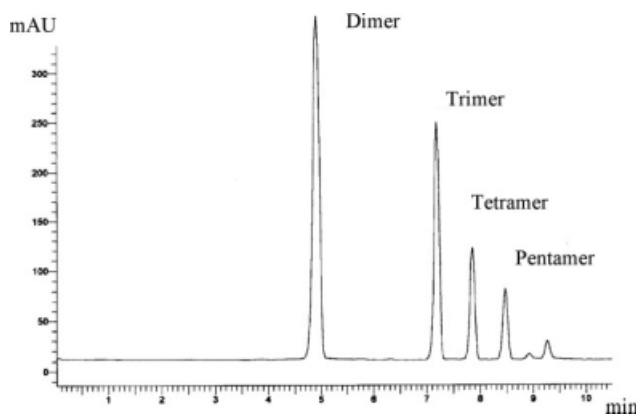


Figure 2 HPLC trace of PBT cyclic oligomers used for the preparation of the nanocomposites. Assignment made by comparison with authentic samples.

Nanocomposite preparation by melt intercalation in Brabender

Blends of standard and telechelic ionic PBT were prepared by melt mixing in a Brabender Plastimeter 2000 equipped with an electrically heated mixer. To ensure the maximum, a 10% overfilling of the mixer was kept for all the mixing experiments. In addition, the fraction of the polymer melt that solidified around the pressure ram used to close the mixer ensuring that moisture did not get in contact with the melt during the mixing process. The mixer was preheated at 250°C and subsequently 62 g of a clay-polyester dry blend (5 : 95 *w/w*) was introduced and mixed at 60 rpm. After 10 min, the polymer melt was taken out from the mixer with the aid of a spatula and allowed to cool to room temperature in air.

Instrumental

Gel permeation chromatography analysis was performed by using a mixture of chloroform hexafluoroisopropanol (95/5 *v/v*) as eluent (elution rate of 0.3 ml min^{-1}) on a HP 1100 Series apparatus equipped with a PL Gel 5 micron Mini-Mixed-C column and a UV detector. Calibration was performed with polystyrene standards.

Differential scanning calorimetry (DSC) analysis was performed using a PerkinElmer DSC7. The instrument was calibrated with high purity standards (indium and phenanthrene). Dry nitrogen was used as purge gas. DSC heating and cooling rate was $20^\circ\text{C min}^{-1}$. All transitions have been measured after a heating scan to 250°C and cooling down to room temperature to delete previous thermal history.

The thermogravimetric analyses (TGA) were performed using a PerkinElmer TGA7 apparatus in air (gas flow: 40 ml min^{-1}) at $10^\circ\text{C min}^{-1}$ heating rate, from 25 to 800°C .

$^1\text{H-NMR}$ spectra were recorded with a Varian XL-400 spectrometer (chemical shifts are downfield from TMS), using a $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (1/4 *v/v*) mixture as solvent. The spectra have been recorded just after dissolution to avoid esterification reaction of end groups with trifluoroacetic acid.

The Wide angle X-ray scattering (WAXS) data were collected with an X'PertPro diffractometer, equipped with a copper anode (K_α radiation, $\lambda = 1.5418 \text{ \AA}$). The data were collected in the 2θ range

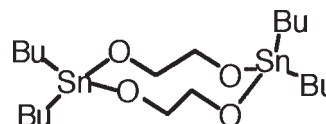


Figure 3 1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxy-acyclodecane) polymerization catalyst.

TABLE I
Polymers and Nanocomposites Obtained by ROP of Cyclic Oligomers and Comparison with PBT 195 and its Nanocomposite Obtained by Melt Intercalation

Sample	Matrix	Clay Added	Reaction Temperature (°C)	Unreacted Cyclics	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)
1	PBT195	–	205°C	–	54,100	26,300
2	PBT195	Dellite 72T	205°C	–	44,500	19,300
3	Cyclic PBT	–	205°C	1%	94,700	43,000
4	Cyclic PBT	Dellite HPS	205°C	2%	106,200	45,300
5	Cyclic PBT	Dellite 72T	205°C	2%	102,000	40,600
6	Cyclic PBT	Dellite 72T	210°C	1%	97,000	36,200
7	Cyclic PBT	Dellite 72T	195°C	4%	108,000	33,000

Five percent by weight of clay.

5–60° by means of an X'Ceerator detector. The d -spacing was calculated using the Bragg's law. In some cases when the d -spacing was over 2 nm, the d -spacing was calculated¹ using the secondary diffraction peak (0.0.2) instead of the main peak (0.0.1).

TEM analyses were performed using a JEOL JEM 2010 instrument.

DMTA analyses were performed with a Rheometrics dynamic mechanic thermal analyzer DMTA 3E with a dual cantilever testing geometry. Typical test samples were bars that were injected molded at 275°C using a Minimax Molder (Custom Scientific Instruments) equipped with a rectangular mold (30 × 8 × 1.6 mm³). The testing was done at a frequency of 3 Hz and temperature range was from –50 to 200°C at a rate of 3°C min⁻¹.

RESULTS AND DISCUSSION

The PBT cyclic oligomers were synthesized using the pseudo-high dilution method reported by Brunelle.³¹ A 5% of ethylene terephthalate moieties were present in the oligomers to decrease their melting temperature. The oligomers were mainly composed by dimers, trimers, tetramers, and pentamers with an average degree of polymerization of 3 as reported in the HPLC trace in Figure 2.

The polymerizations of cyclic oligomers have been conducted, after purification, using trimethyl-orthoacetate as capping agent for the reduction of COOH end groups following the procedure developed by Brunelle³³ using 0.3 mol % of a cyclic stannoxane (1,1,6,6-tetra-*n*-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane) (Fig. 3) as catalyst.

The amount of catalyst and the addition of the capping agent are of fundamental importance to achieve high-molecular weight polymers. Indeed, using this polymerization procedure PBT samples having M_w over 100,000 have been obtained (Table I), whereas polymers with M_w of 34,500 have been obtained using titanium butoxide as catalyst. Again, the maximum molecular weight obtained without the addition of the capping agent and with cyclic

stannoxane catalyst was 35,000. The addition of ortho-esters reduces the amount of carboxylic acid groups that are present in linear oligomers impurities in the starting cyclic oligomers. The carboxylic acid moieties inhibit the catalytic activity of titanium and tin based catalysts and also acts as chain stoppers. For these reasons most of the previous works reported in the literature^{26–29} did not succeed in obtaining high M_w nanocomposites. M_w of 146,000 can be obtained decreasing the catalyst content to 0.15 mol %, since no side reaction occurs and the end groups are only due to the catalyst that acts as chain-ender. Indeed, no OH or COOH end groups have been detected by ¹H-NMR analyses and COOH end-group titrations. No other signals due to side reactions (e.g., vinyl groups) were detected by ¹H-NMR analyses (Fig. 4).

After the catalyst addition, the polymerization is very fast and within 15 s the molten cyclic oligomers become too viscous to be mechanically stirred. Crystallization of the polymer usually occurs within 5 min and the reaction mixture was kept reacting in the solid state for additional 5 min. The reaction temperatures and the stirring are very important to have a low polydispersity and an amount of unreacted cyclic oligomers below 2%. Indeed, it is important to well disperse the catalyst in the reaction mixture before the reaction mixture become too viscous. If the temperature is too low the

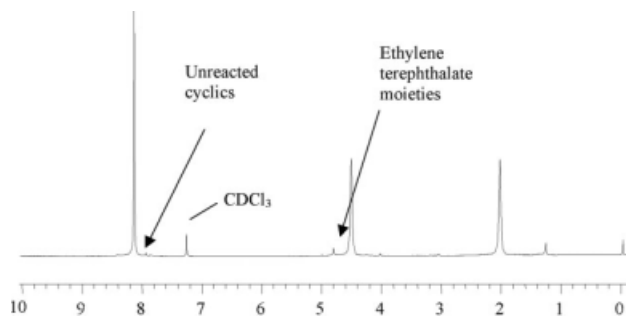


Figure 4 ¹H-NMR after polymerization of PBT cyclic oligomers.

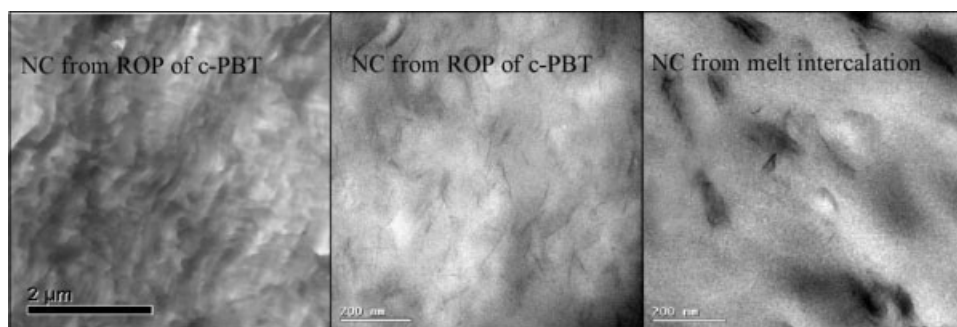


Figure 5 TEM analysis of nanocomposites made with Dellite 72T from ROP of c-PBT and from melt intercalation.

crystallization occurs very rapidly, thus not allowing the polymerization to proceed at sufficient rate, since the solid state polymerization is consistently slower respect to the polymerization in the melt and therefore consistent amount of unreacted cyclics (4%) are left in the final material working at 195°C (Table I). Moreover, the polydispersity at 195°C is larger respect to that obtained at 205 and 210°C. On the contrary, at higher temperatures (210°C), polymerization occurs too fast thus preventing the good dispersion of the catalyst. Indeed at 210°C, a larger polydispersity respect to 205°C has been observed. Moreover, at higher temperatures side reactions can occur, limiting the molecular weight of the polymers. We have found that 205°C is the optimal reaction temperature since the unreacted cyclic oligomers level (that strongly affects the thermomechanical properties) is below 2% (as detected by $^1\text{H-NMR}$) and the polydispersity is 2.2.

We have found that the addition of an organically modified clay and of the pristine clay does not influence the ROP of the cyclic oligomers (Table I). Polymers with high M_w (above 100,000) and <2% of unreacted oligomers have been obtained in the presence of 5% *w/w* of a MMT modified with a quaternary ammonium salt bearing two hydrogen tallow and two dimethyl groups (Dellite 72T from Laviosa Chimica Mineraria, Italy). To the best of our knowledge, it has never been reported the preparation of PBT nanocomposites with M_w above 100,000 by the melt intercalation or *in-situ* polymerization approaches since the very high-reaction temperature and the low stability of the ammonium modified clays give rise to a consistent molecular weight drop. In particular, we have observed for the nanocomposites obtained by melt intercalation, used as comparison in this study, a 15–20% drop of molecular weight. Indeed, the onset degradation temperature (by TGA at $10^\circ\text{C min}^{-1}$) of Dellite 72T is 278°C and a 4% weight loss was observed after 5 min at the processing temperature of PBT (250°C).

The TEM micrographs of the nanocomposites obtained by ROP and by melt intercalation are

reported in Figure 5. It is possible to notice the improved dispersion using the ROP process. By this method mostly exfoliated morphology can be achieved, whereas with the melt intercalation process large tactoids formed of several clay platelets are present. Larger tactoids are present when a pristine clay is used. Moreover, the polymer melt is opaque when a pristine MMT is used, whereas it is perfectly transparent when the organically modified clay is used indicating, again, that a modified clay must be used (Supporting information available with online version).

The XRD analyses (Fig. 6) of the oligomers mixed with the clay for 1 h at 205°C before the catalyst addition show that the cyclic oligomers intercalates the MMT platelets (the *d*-spacing calculated using the Bragg's law increases respect to starting MMT from 2.4 to 2.8 nm). The rapid polymerization of the cyclic oligomers produces the disintegration of the layered silicates since almost no reflection is present in the WAXS spectra of the final composite. On the contrary, a significant reflection is present for a *d*-spacing of 3.4 nm for the nanocomposite obtained by the melt intercalation route (Fig. 7). These results clearly indicate a better dispersion of the clay in the nanocomposite obtained by ROP.

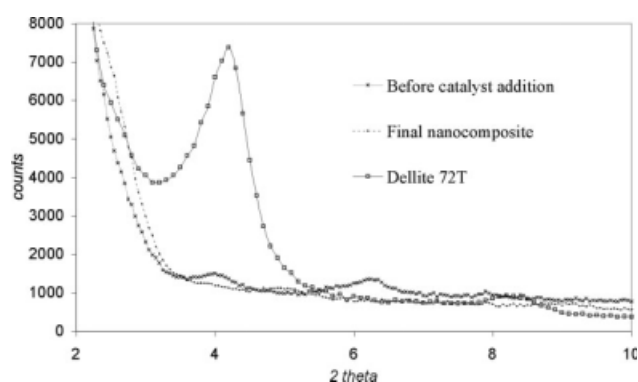


Figure 6 XRD of c-PBT/Dellite 72T before and after catalyst polymerization.

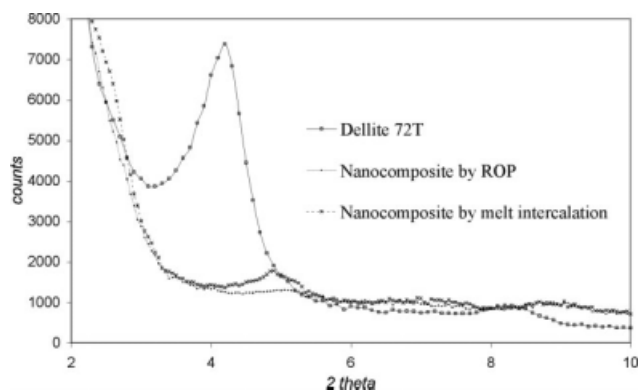


Figure 7 XRD comparison of nanocomposites made by *in-situ* polymerization using c-PBT and by melt-blending using standard PBT.

The DMTA analysis (Fig. 8) shows an improvement of the thermomechanical properties for the nanocomposites respect to a commercial PBT sample (Valox195 from General Electric Plastics) above the glass transition temperature. This improvement is more consistent for the nanocomposites prepared by ROP respect to those obtained by melt intercalation. According to a procedure originally proposed by Takemori,³⁹ DMTA data can be used to estimate the HDT. The commercial PBT Valox195 has an HTD at 120°C (under 0.45 MPa static load) and at that temperature the storage modulus (E') measured by DMTA was 2.5×10^8 Pa. The nanocomposite obtained by melt intercalation showed that value of modulus at 141°C, the composite made with cyclics and pristine MMT 137°C and the nanocomposite obtained by ROP of cyclic oligomers at 154°C. These differences were attributed to the more efficient dispersion of the clay platelets using the ROP approach. The improvement in the storage modulus above

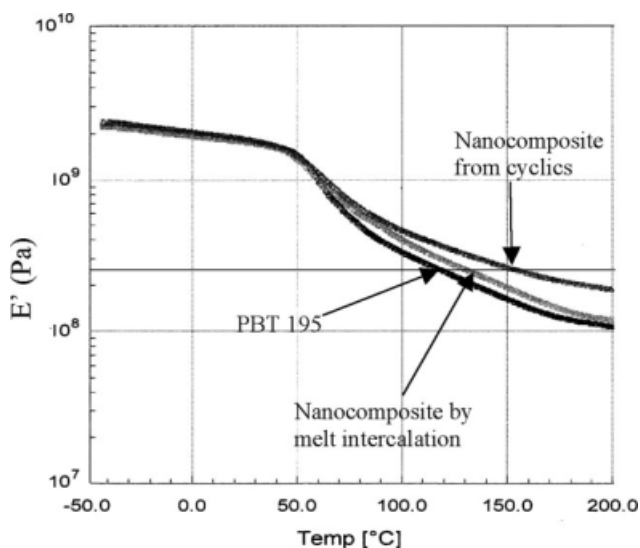


Figure 8 Comparison of nanocomposites made by melt blending and by *in-situ* polymerization using Dellite72T.

TABLE II
Thermal Properties of Polymers and Nanocomposites Obtained

Sample	Matrix	Clay Added	T_m (°C) ^a	ΔH_m (J g ⁻¹)	T_c (°C)
1	PBT	–	222.7	42.8	183.3
2	PBT	Dellite72T	221.4	38.2	183.3
3	c-PBT	–	223.1	78.4	184.5
4	c-PBT	Dellite HPS	225.4	73.2	185.1
5	c-PBT	Dellite72T	224.2	69.4	183.4

^a T_m and ΔH_m have been measured in the first heating scan at 20°C min⁻¹.

glass transition temperature gives rise to an increase in the HDT and therefore to the possibility to use the material in a wider range of temperatures.

The result of DSC analysis (Table II) shows no significant differences in crystallization temperatures and in melting temperatures comparing the nanocomposites with the commercial PBT. A higher degree of crystallinity has been observed for the polymers obtained from cyclic oligomers according to the literature.³³ No significant differences in thermal stability by TGA analysis in air has been observed.

CONCLUSION

The ROP of PBT cyclic oligomers in the presence of organically modified MMT represents a very attracting route for the preparation of nanocomposites. The ROP occurs in very short reaction times (10 min) at lower temperatures (205°C) respect to the standard melt intercalation route. Very high-molecular weight can be obtained using a capping agent and the proper catalyst amount and reaction temperature.

The main advantages of this method respect to melt intercalation approach are the higher molecular weight achievable, the highest purity of the polymer, the higher degree of dispersion of the clay and the better overall thermomechanical properties.

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