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A new solid-state process for chemical modification of PET for crystallization rate enhancement

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Abstract

It was recently shown that the crystallization rate of poly(ethylene terephthalate) (PET) can be enhanced by introduction of diamide units either by use of comonomer during polymerization, or during a subsequent extrusion process. Here, we demonstrate an alternative solid-state chemical modification process where the amide groups are introduced into commercial PET by exposing the PET pellets simply to vapors of ethylene diamine at 125 °C, i.e. far below the melting point of PET. We make up for the corresponding decrease in molecular weight by a subsequent solid-state polymerization. We find that the crystallization rate enhancement is at least comparable to that achieved by using talc as nucleating agent. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Solid-state; Modification

1. Introduction

Poly(ethylene terephthalate) (PET) is widely used as films and fibers. However, its application as an engineering plastic for injection molding applications is rather limited. This is due to the slow crystallization rate and hence large cycle time for PET as compared to poly(butylene terephthalate). Due to the cost advantage offered by PET, many reports describe the search for nucleating agents or crystallization promoters for PET [1]. An industrially used nucleating agent is talc, which is also often the benchmark for future improvements. Other nucleating agents/promoters that have been reported are ionomers, metal oxides and hydrides, many organic compounds, residual catalysts, polymers and fibers. The group at Twente recently achieved crystallization rate enhancement in PET by introduction of diamide units by use of a specially synthesized comonomer (dimethyl (N,N' bis(p-carbomethoxybenzoyl) ethanediamine)) either during polymerization [2], or during a subsequent extrusion process [3]. Nakano and Kato [4] used a solution process to produce polyamide from PET and hexamethylene diamine. Ukita et al. [5] reported nitrogen incorporation in 15 μm diameter PET fibers by reaction with ethylene diamine (EDA) vapors. Presence of water

vapor was required, perhaps for creation of acid end-groups for amidation reaction. At 120 °C and lower, the reaction seemed limited to the surface (1–2 μm depth). Deeper penetration was facilitated at 190 °C by the cracks formed in the fibers. In this communication, we describe a solid-state process for EDA incorporation as amide segments into commercial PET *pellets*, without melting, and without using water or diluents. We also follow the changes in the molecular weight, and influence on crystallization characteristics.

2. Experimental part

2.1. Materials

PET pellets are the commercial BAGA grade ($\eta_{inh} = 0.62$ dl/g, characteristic cylindrical diameter 2.5 mm, length 3 mm), synthesized by the dimethyl terephthalate route, and supplied by Acordis. EDA was obtained from Aldrich, and used after drying with molecular sieves.

2.2. Process

The PET pellets (15 g) were filled in a wire-net bucket placed in a two-neck flask (Fig. 1). To one neck of the flask,
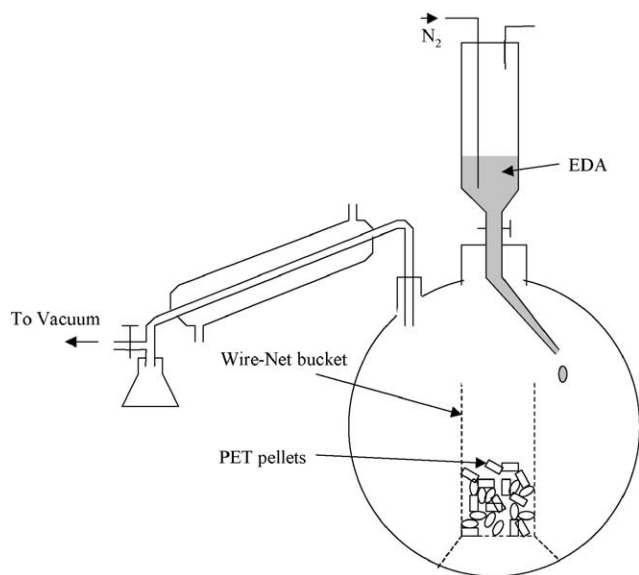

Fig. 1. Schematic of apparatus for solid-state modification.

we attached a dropping funnel containing EDA, and to the other neck we attached a condenser–receiver unit with connection to vacuum pump (Fig. 1). Vacuum (9 mm Hg) was applied and the flask was heated to 125 °C for 1 h to dry the PET pellets. After disconnecting the vacuum, EDA (2 ml) was added to the flask slowly as drops. The drops vaporized as they fell on the heated flask bottom, and the vapors contacted the PET pellets by convection through the wire-net bucket. Excess EDA vapors continued to the condenser/receiver. After 5 min of exposure to EDA vapors, vacuum was applied again, to remove the unreacted EDA. The temperature was raised and maintained at 210 °C for 1 h to enable polycondensation and exchange reactions. The pellets were withdrawn after cooling and release of vacuum. These pellets were homogenized by extrusion with a corotating twin-screw mini-extruder at 275 °C (4 cc capacity DSM Model RD11H-1009-025-4) into 1 mm diameter strands (sample PET_EDA-1). Further solid-state polymerization (SSP) of the strands was carried out at 220 °C under nitrogen flow, and samples were withdrawn at 7 h (sample PET_EDA-2) and 14 h (sample PET_EDA-3).

For comparison, the as-received pellets were also mixed with talc powder (0.3 wt%) and extruded at 275 °C (sample PET_Talc).

2.3. Characterization

The extent of EDA incorporation was determined by measuring nitrogen content using a CHN analyzer (Perkin–Elmer Series II CHNS/O analyzer, model 2400). Proton NMR were recorded on a Varian Mercury Vx 400 spectrometer at 400 MHz, using deuterated trifluoroacetic acid as a solvent. The weight average molecular weight (M_w) and polydispersity index (PDI) were determined by GPC analysis using polystyrene standards and 5% hexafluoroisopropanol in chloroform as eluent. Inherent viscosity (η_{inh}) measurements were done at 0.5 g/dl in 50/50 (w/w) mixture of phenol–tetrachloroethane at 30 °C.

The crystallization characteristics of the samples were examined using Perkin–Elmer differential scanning calorimetry system DSC-7. The melt crystallization temperatures (T_c) were determined in the following manner: the PET was first heated at 100 °C min^{-1} to 310 °C, maintained there for 10 min to eliminate the thermal and shear history effects, and then cooled at 20 °C min^{-1} to 150 °C. The peak in the crystallization exotherm was taken as the crystallization temperature (T_c). Isothermal crystallization experiments involved heating the samples at 100 °C min^{-1} to 310 °C, and maintaining there for 10 min, and then cooling at 100 °C min^{-1} to the desired isothermal crystallization temperature ($T_{iso} = 210, 215, 220$ or 225 °C). The samples were maintained at T_{iso} for 4 min during which the isothermal crystallization characteristics are recorded. The time corresponding to maximum in the heat flow rate ($\propto$ crystallization rate) was taken as t_{peak}.

3. Results and discussion

Table 1 gives a description of the samples and their characterization. We study the relative crystallization behavior of the modified samples to examine the influence of incorporation of the amide segments. Since shear and thermal history during the process can affect the crystallization behavior [6,7], elimination of such effects is crucial. Comparison of the PET_Extrusion sample with PET (Table 1) shows that the increase in T_c due to the extrusion step is small (2 °C). This is because we maintained the samples at 310 °C for 10 min to eliminate the history effects before the
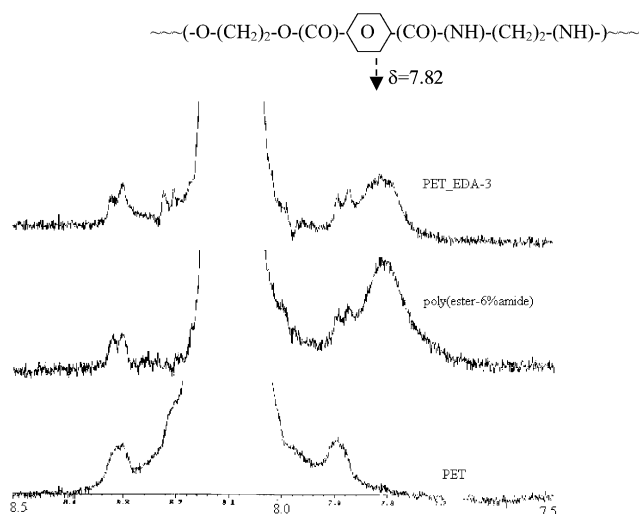
Table 1
Details of the PET and modified samples

No.	Sample	History	η_{inh} (dl/g)	M_w	PDI	N (%)	T_c (°C)
1	PET	As-received	0.62	61 200	2.7		198
2	PET_Extrusion	PET after extrusion	0.50	41 200	2.1		200
3	PET_EDA-1	PET + EDA vapor rxn + extrusion	0.37	26 000	2.5	0.31	216
4	PET_EDA-2	PET_EDA-1 + 7 h SSP	0.54				
5	PET_EDA-3	PET_EDA-1 + 14 h SSP	0.61	74 400	2.9	0.31	213
6	PET_Talc	PET extrusion with 0.3% talc	0.51	41 700	2.5		210

~~~(-O-(CH$_2$)$_2$-O-(CO)-⟨O⟩-(CO)-(NH)-(CH$_2$)$_2$-(NH)-)~~~

↓ δ=7.82

Fig. 2. NMR spectra of PET (as-received) and modified samples.

Fig. 3. DSC cooling scans of PET (as-received) and modified samples.

cooling scan in DSC during which T_c was recorded. The small increase can be attributed to the decrease in molecular weight during melt extrusion.

The presence of nitrogen to the extent of 0.31 wt% (2.2 mol% amide, assuming all N is present as amide) in sample PET_EDA-1 and PET_EDA-3 indicates that EDA indeed gets incorporated from the vapors into the polymer molecules in the PET pellets during the solid-state reaction. This is further confirmed by NMR of the PET_EDA-3 (Fig. 2). The chemical shift of the protons on the phenyl rings with amide side is lower (δ = 7.82 ppm, Fig. 2) as compared to (δ = 8.1 ppm) for protons on the phenyl rings with ester sides. Though the resolution of the δ = 7.82 ppm peak from the neighboring peaks is limited, its area (∼2% of the large δ = 8.1 ppm peak) compares well with the estimate from elemental analysis. The limited accuracy of this peak integration does not allow us to exclude the possibility that some of the amine functionality may be present due to EDA incorporation at chain ends. That the δ = 7.82 ppm peak is indeed due to the links of phenyl rings to amide functionality, is confirmed by the NMR spectra (Fig. 2) of the polyesteramide (6 mol% amide) made by the comonomer route as described in Ref. [2].

3.1. Effectiveness of PET modification in crystallization rate enhancement

Fig. 3 shows the DSC scans of the as-received PET, and some modified PET samples. During cooling from melt, the EDA or the talc modified PET samples show crystallization exotherms earlier than the as-received PET, as also indicated by the T_c values in Table 1. This indicates that both the amide segments and the dispersed talc are effective as nucleation/crystallization promoters, the former being somewhat better. The extent of increase in T_c by about 10–15 °C in both cases is comparable to the effect of previously reported nucleating additives such as talc [3,6], amide [2,3]
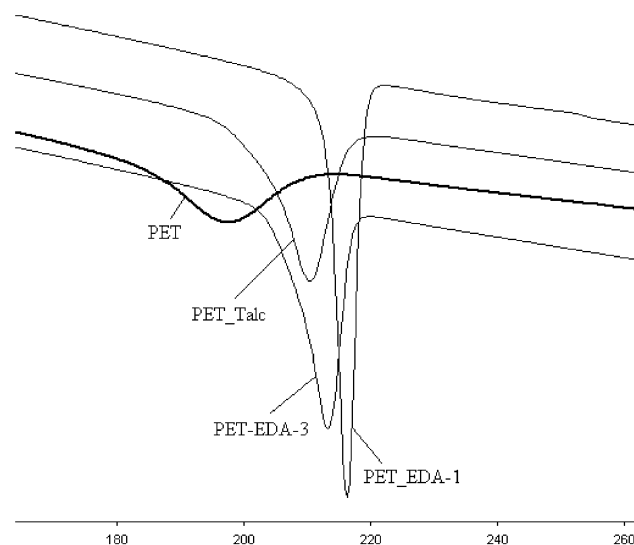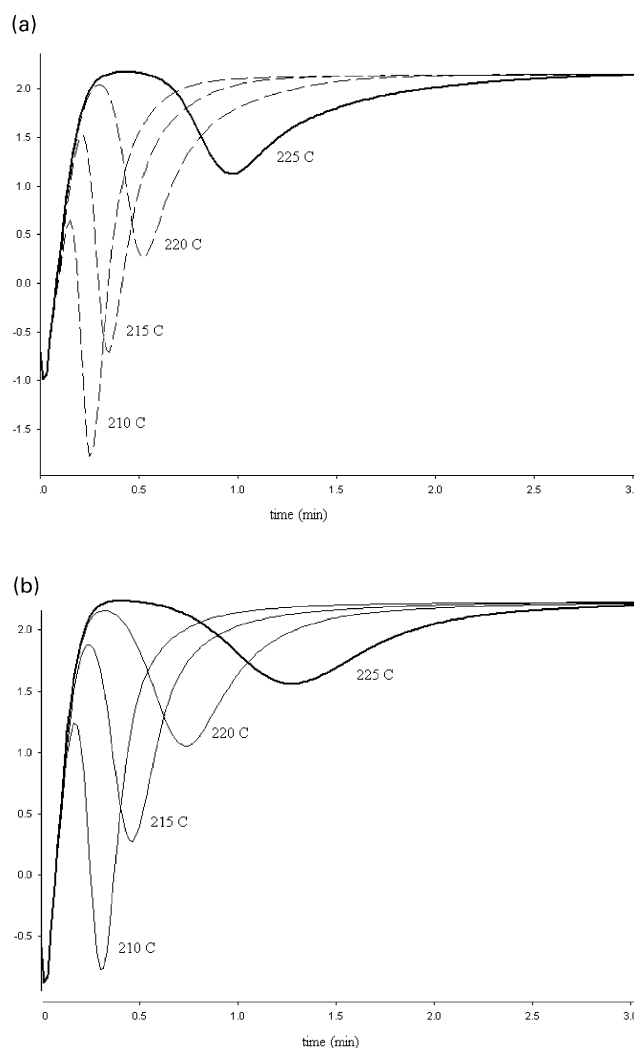

Fig. 4. Heat flow during isothermal crystallization (DSC) for (a) PET_EDA-2 and (b) PET_Talc at different T_{iso}.
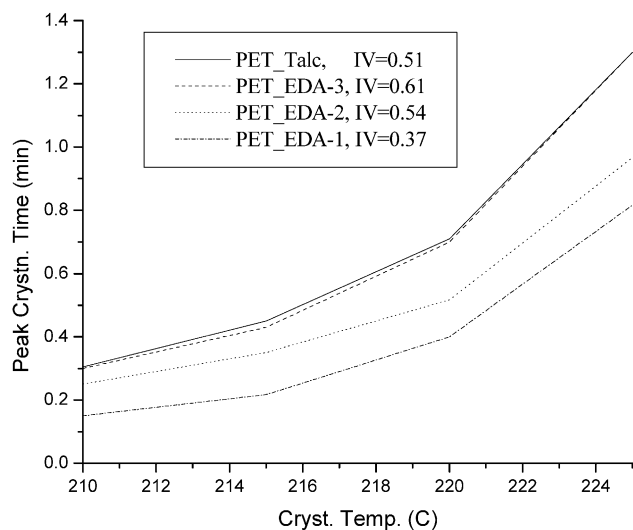
Fig. 5. Effect of molecular weight of modified PET on peak crystallization time (t_{peak}) DSC at different temperatures (T_c).

and ionomers [8]. This suggests that satisfactory dispersion of talc and incorporation of amide into the PET chains has been achieved in our mini-extruder. While Bouma and Gaymans [3] found 0.1 mol% amide incorporation to be less effective than 0.5 wt% talc in enhancing T_c, we find that 2.2 mol% amide incorporation by the solid-state reaction is at least as effective as 0.3 wt% talc incorporation.

Fig. 4 shows the results of isothermal crystallization experiments for samples PET_EDA-2 and PET_Talc of comparable molecular weight. The smaller t_{peak} values for PET_EDA-2 as compared to PET_Talc (Fig. 5) suggests faster crystallization of the amide (2.2 mol%) containing PET as compared to talc (0.3 wt%) containing PET.

3.2. Effect of molecular weight

Examination of Table 1 shows that the T_c of the amide modified PET decreases somewhat with increase in molecular weight. This confirms the well-known effect of decreasing crystallization rate with increasing molecular weight [9]. This effect is also seen in the isothermal crystallization experiments at different temperatures, T_{iso}. The results of different molecular weight PET_EDA consolidated in Fig. 5 show that crystallization takes longer (higher t_{peak}) for PET_EDA of higher molecular weights.

4. Conclusions

We have presented a new diluent-free solid-state process for chemical modification of pellets of condensation polymers. Commercial PET pellets are directly exposed to vapors of reactive functional monomers. On diffusion into the polymer pellets, the functional monomer can undergo reaction with the $-COOH$ and $-OH$ functionalities at chain ends, or with the $-O-(CO)-$ functionality along the chains. Besides, exchange reaction can aid the distribution of the comonomer so incorporated. As expected, molecular weight of the polymer decreases, but can be built up to the original level by a subsequent SSP. Since the process neither involves melting or dissolution of the pellets until they are ready for compounding, nor does it involve a solvent or a diluent for dissolution of the functional monomer, the economical and environmental advantages of the solid-state modification process are clear. We here demonstrated that such a process can indeed effectively incorporate amide segments to the extent of 2.2 mol% in commercial PET. We find that the amide functionality so incorporated is effective in enhancing the crystallization rate of PET, sufficiently to substitute talc as a nucleating agent.

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