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Reactive processing of poly(ethylene terephthalate) modified with multifunctional epoxy-based additives

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Abstract

The use of multifunctional epoxy-based modifiers to increase the melt strength of poly(ethylene terephthalate) (PET) has been investigated, with the aim of producing PET foams by an extrusion process. The reaction conversion has been studied as a function of time by the measurement of torque in an internal mixer. A tetraglycidyl diamino diphenyl methane (TGDDM) resin was selected for the investigation of the modifier concentration effect on the reaction conversion. Using a stoichiometric concentration of TGDDM, the molecular weight distribution of modified PET, as determined by gel permeation chromatography (GPC), showed an eight-fold increase of the *z*-average molecular weight (M_z) and the presence of branched molecules of very large mass. The resulting intrinsic viscosity of the modified PET was 1.13 dl/g. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Epoxy-additives; Reactive processing

1. Introduction

The foaming of poly(ethylene terephthalate) (PET) is of great interest for the production of insulation panels and core components for sandwich structures. In the past decade, several studies have shown that a high melt strength of the PET is required in order to avoid the collapse of the foam structure during the stabilisation phase of the cell growth [1]. This is of particular importance for an extrusion process, since foaming induces rapid and large extensional deformations and thus the material requires a high extensional viscosity [2]. The use of recycled PET in such durable applications of high value is at present limited because of the material's limited melt strength. This results mainly from the molecular weight drop enhanced by repeated processing operations during which the absorption of moisture leads to a rapid degradation reaction in the condensation polymerised polymer.

The melt strength usually depends on three molecular characteristics, which are the molecular weight average (M_w) related to the chain length, the molecular weight distribution (MWD) and the degree of branching. To obtain a higher melt strength, several techniques based on chain lengthening have been reported, among which solid-state polycondensation (the SSP process) is the most used. Degradation is avoided since SSP is performed in the solid state; however, it is diffusion-controlled and as such it is a rather long process. As an alternative, reactive processing with shorter thermal cycles has been carried out with a variety of additives to induce chain lengthening. Bifunctional molecules such as diepoxides, diisocyanates, dianhydrides or bis(oxazoline)s have been shown to react with terminal groups of PET, [3,4] with a corresponding increase in molecular weight. Pyromellitic acid dianhydride (PMDA) was found to increase significantly the intrinsic viscosity to a level that allows the manufacture of foams [5]. Cardi et al. [4] used 2,2″-bis(2-oxazoline) and obtained an eight-fold increase of the apparent viscosity. Triphenyl phosphite [6,7] as well as diimidodiepoxides developed by Bikiaris et al. [8] have also shown an efficient reactivity with PET.

In all of these cases, reactive extrusion requires close control of the process due to competing poly-condensation and degradation reactions, for which reaction by-products and the overall moisture content must be minimised. With this in view, the most appropriate molecules would promote addition reactions while avoiding by-products such as water, which induce degradation at high conversions. The modifier structure and size must also be taken into account to ensure the solubility required within PET for efficient reactivity. Since PET processing is performed in vicinity of 300°C, the thermal stability and homopolymerisation of

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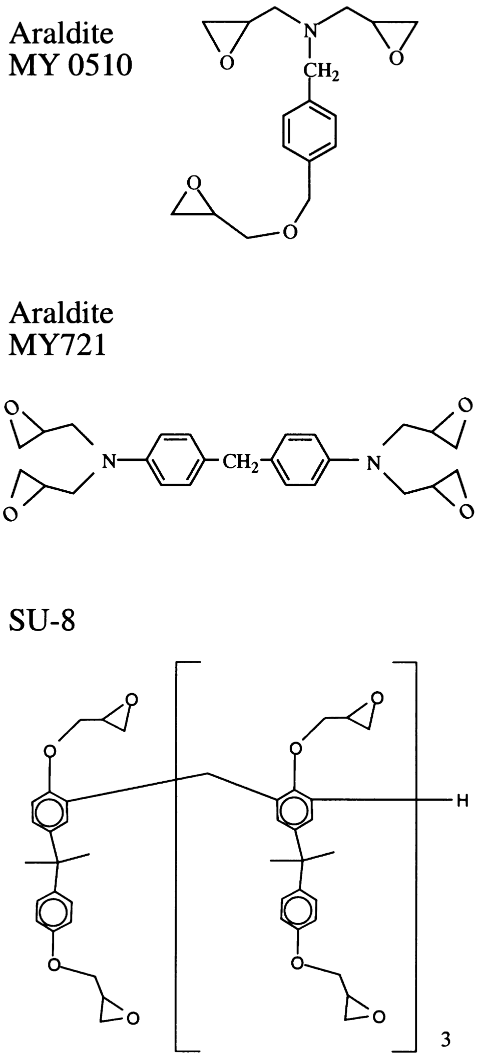

Fig. 1. Commercial epoxy-based modifiers [28].

the modifier must further be determined. Multifunctional structures are of interest since they are thought to increase the reactivity and induce long chain branching, which is believed to result in an extension-thickening behaviour and concomitant increase of the extensional viscosity [9]. Multifunctional epoxides offer a combination of all these parameters and have been selected in this study.

Gel permeation chromatography (GPC) provides a high resolution method for determining molecular weight distributions [10–12]. The coupling of different molecular weight-sensitive detectors makes GPC a very powerful tool for the detection of long-chain branching in polymers as shown by Lesec et al. [13], including that of low-density polyethylene [14,15].

The purpose of the present investigation is to study the reactivity of PET with tri-, tetra- and octo-functional epoxy-based modifiers and to characterise the modified molecular architecture in terms of: (i) the rheology of the modified polymer; and (ii) its branched structure.

2. Experimental

2.1. Materials

A PET copolymer (bottle-grade Eastman 9921W) was used. It is produced from dimethyl terephthalate and ethylene glycol and is characterised by an intrinsic viscosity (IV) of 0.81 dl/g, a weight-average molecular weight (M_w^{PET}) of 52,000 g/mol and a number-average molecular weight ($\overline{M}_n^{PET}$) of 26,000 g/mol. The measured carboxyl and hydroxyl contents are 15 and 60 μmol/g, respectively.

Three commercial multifunctional epoxide modifiers were selected, the structures of which are shown in Fig. 1. 4-glycidyloxy-*N*,*N*′-diglycidaniline (Araldite MY 0510, Ciba SC) is a low viscosity tri-functional resin with an epoxy equivalent weight (EEW) of 102.7 g/equiv. Tetraglycidyl diamino diphenyl methane (TGDDM) (Araldite MY 721, Ciba SC) is a tetra-functional resin with a theoretical EEW of 105.5 g/equiv. (measured EEW of 111.5 g/equiv). The glycidyl ether of bisphenol A Novolac resin (Epon resin SU-8, Shell Chemical Company) has a high epoxy functionality of eight and a theoretical EEW of 174.7 g/equiv. (measured EEW of 216 g/equiv).

2.2. Reactivity characterisation

2.2.1. Thermal stability of modifiers

It is necessary to determine whether during the reactive extrusion process of PET with a modifier, the latter homopolymerises instead of reacting with PET, which would modify its functionality and branching efficiency.

The thermal stability of epoxy modifiers was analysed by means of differential scanning calorimetry (DSC-7, Perkin–Elmer). The reaction enthalpies were measured using a temperature scan at a rate of 5 C/min. Isothermal tests were also run at 270°C, corresponding to the reactive processing temperature, to characterise the autocatalytic reaction kinetics of homopolymerisation.

2.2.2. Reactivity with PET

Aharoni et al. [6] used model molecules to investigate the reactivity between carboxyl PET chain end groups and triphenylphosphite (TPP). In this study, two other model molecules representative of PET chain ends were selected, as depicted in Fig. 2. These allow to differentiate between the reaction of carboxylic acid and hydroxyl groups with epoxy, since epoxy groups are known to react differently with –COOH and –OH groups [8,16]. The carboxylic chain end model molecule is 4-ethylbenzoic acid and the hydroxyl chain end model molecule is 2-(4-methoxyphenyl) ethanol, which were chosen due to their similarity to a PET chain end.

The thermal properties of the model molecules define the temperature limits for thermal reactions, which can be characterised using this approach. The melting point of

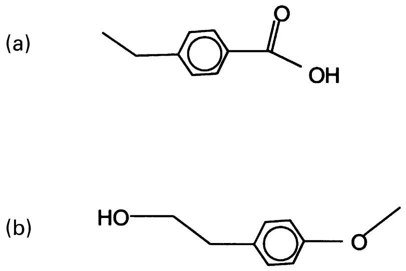

Fig. 2. Model molecules:(a) 4-ethylbenzoic acid; (b) 2-(4-methoxyphenyl) ethanol.

4-ethylbenzoic acid is 114°C and degradation starts at 220°C. The thermal stability limit of 2-(4-methoxyphenyl) ethanol, liquid at room temperature, is 190°C, at which temperature volatilisation initiates.

The mixing ratios were calculated based on the epoxy functionality values yielding ratios of 3.0:1, 3.78:1 and 6.47:1 of the model-molecules to the MY0510, MY721 and SU-8 epoxy resins, respectively. After manual mixing, the samples were tested in DSC at a 10°C/min temperature scan to determine the exothermic peak of reaction. The reactivity of each epoxy group for the three different resins was analysed using isothermal tests run at the measured exothermic peak temperature and characterised by the resulting isothermal peaks.

2.3. Reactive processing

Reactive processing was studied by shear mixing in a Brabender Plasticorder torque rheometer equipped with two counter-rotating screws and a capacity of 50 ml. Reactive extrusion was performed using a co-rotating twin screw extruder (PRISM TSE 16). PET and modifiers were dried in a vacuum oven to reduce the moisture content to less than 50 ppm [17]. To this end, PET was dried at 150°C during 6 h at least; modifiers were dried at 40–50°C during 24 h.

The stoichiometric amount of modifier added to the PET was calculated considering a functionality of one for each PET molecule. Assuming that only carboxyl groups react with epoxy groups, since these are the most reactive and short residence times are used in reactive extrusion, this would imply that each PET chain had on average one carboxyl group. This is, however, not the case for the virgin material but degradation must be considered since this can occur rapidly and preferentially creates new carboxyl groups [1]. It was found that the COOH content was doubled after a 2 min residence time in the extruder. Thus, as an average, one mole of PET was assumed to react with 1/*f* mole of modifier, *f* being the real functionality of the modifier. The theoretical stoichiometric amount of modifier is therefore:

$$w = \frac{M_{\mathrm{w}}^{\mathrm{m}}}{f \overline{M}_{\mathrm{n}}^{\mathrm{PET}}} \qquad (1)$$

Table 1
Calculated values of real stoichiometric concentration according to Eq. (1)

Modifier	$M_{\mathrm{w}}^{\mathrm{m}}$ (g/mol)	Real functionality	Stoichiometric concentration (wt%)
MY721	422	3.78	0.43
MY0510	305	3	0.39
SU-8	139l	6.47	0.83

where $M_{\mathrm{w}}^{\mathrm{m}}$ is the molecular weight of the modifier and $\overline{M}_{\mathrm{n}}^{\mathrm{PET}}$ the number-average molar mass of PET. The calculated values for the three epoxy resins are given in Table 1.

MY0510 and SU-8 have been tested at stoichiometric concentrations and MY721 at four different concentrations in the Brabender (0.2, 0.25, 0.4 and 0.5 wt%). Samples weighing 62 g were loaded into the mixing chamber of the torque rheometer and reactive mixing was carried out at 270°C and 40 rpm.

For reactive extrusion, the temperatures were set to 220°C at the feeder, to 270°C at the centre and to 250°C at the die. The speed was set to 50 rpm and the residence time was defined by the feeding rate (approximately 40 ± 5 s). The extruded material was cooled at room temperature, pelletised and finally dried. A second extrusion of this material was performed under the same conditions.

2.4. Molecular architecture characterisation

2.4.1. Intrinsic viscosity and COOH content

Intrinsic viscosity measurements were performed using the Ubbelohde tube method described in DIN 53728. In this technique, dried PET is dissolved at 0.5% in phenol/1,2-dichlorobenzene and measurements are carried out at 25°C. The COOH content of the blends was analysed with an automatic pH titration method [18].

2.4.2. Molecular weight distribution

The MWD measurements were performed using a Multidetector GPC Waters 150-CV equipped with four columns (Styragel HR-$10^6/10^5/10^4/10^3$ Å) and connected to a refractometer coupled to a viscosimeter. The universal calibration curve obtained with polystyrene was used to calibrate the corresponding molecular weight of PET. The Mark–Houwink relationship was calculated from a curve of the measured viscosity as a function of the corresponding molecular mass [19]. The eluant system used for PET was dichloroethane/hexafluoroisopropanol (95:5) at 30°C.

3. Results and discussion

3.1. Reactivity of epoxy resins with PET

3.1.1. Thermal stability of epoxy resins

The reaction enthalpies of homopolymerisation, indicative of the stability of the epoxy resins, were found to be −387.5 and −457.9 kJ/mol for MY0510 and MY721, respectively. The reaction enthalpy of SU-8 was not determined because degradation was found to occur before homopolymerisation ended. The 270°C isothermal responses of the three epoxies are illustrated in Fig. 3. It is clear that homopolymerisation of MY721 is faster than that of MY0510, which is more thermally stable at 270°C. On the contrary, SU-8 does not homopolymerise at this temperature. In the two former cases, the functionality reduction related to the consumption of epoxy groups was calculated by measuring the reaction enthalpy after 3 min. This would correspond to a conservative estimation of the modifier functionality available for branching, 3 min being longer than the extrusion time, but it should be noted that only a diffusion-controlled reaction occurs in the DSC, contrary to the reactive extrusion. To determine the reaction enthalpy occurring during heating of the DSC, the heat flow was extrapolated using an appropriate curve fit before heat stabilisation. The percentage of reaction was determined by dividing the calculated reaction enthalpy at 3 min by the total reaction enthalpy as measured by the temperature scan. In the case of the MY0510 resin, the above calculation indicates that 5.4% of the total number of epoxy groups have reacted after 3 min. Assuming that statistically only one epoxy group per molecule reacts, 16.3% of all molecules have one epoxy group, which has reacted. Thus, if only dimers are created, 8.2% of molecules are dimers with a functionality of 4. The average functionality per molecule is then 3.09, the average molecular weight is 332.2 g/mol and the EEW is 107.5 g/equiv. In the case of the MY721 resin, after a reaction time of 3 min, 12.3% of the total number of epoxy groups have reacted. Applying the same assumptions, the average functionality per molecule is increased to 4.30, the average molecular weight to 550.0 g/mol and the EEW to 127.9 g/equiv. It should, however, be noted that these results have been obtained for an undiluted system. By contrast, during the reactive process, the resin homopolymerises mainly during the melting stage of PET when its concentration is sufficiently high. Epoxy molecules are then rapidly dissolved in the PET phase and thereafter preferably react with carboxylic acid groups, as will be shown in the following section. Nevertheless, the determination of the true average functionality of the modifier, which will be in between the true functionality of the unreacted modifier and those determined here, can play an important role for the structural analysis of the modified PET. The consequence of homopolymerisation will thus be to increase the number of reactive groups per molecule and to induce a broadening of the molecular weight distribution.

3.1.2. Modifier-PET reactivity

The reactivity of 4-ethylbenzoic acid with epoxy was found to be very similar for the MY721 and MY0510 in DSC temperature scans. A slight shift was observed in the exothermic peak (135 and 137°C), due to an observed better solubility of the 4-ethylbenzoic acid in MY0510 than in MY721. On the other hand, the exothermic peak of SU-8 resin and 4-ethylbenzoic acid was found to occur at 200°C. This reaction is, however, much slower and again indicates a reduced reactivity. Isothermal reaction thermograms performed at the respective peak temperatures are shown in Fig. 4.

In all the three cases, the reaction between carboxylic acid and epoxy groups is prominent and fast. The enthalpy energies per epoxy equivalent, as determined from the area under the curves in Fig. 2, are similar for SU-8 and MY0510 and close to 70 J/equiv., whereas that for MY721 is 60 J/equiv. However, a refined examination reveals two reaction kinetics in the case of SU-8, which was reacted at higher temperatures. The first reaction is common to the three modifiers, and corresponds to the reaction of COOH with epoxy, creating an OH group. At 200°C, the latter can further induce secondary kinetics due to either a direct reaction with the epoxy or a catalytic effect on the carboxyl–epoxy reaction. The reaction enthalpy of MY721 was expected to be similar to the MY0510 case since the epoxy group structure of both molecules is very similar. The observed difference of 14% could arise from a faster reaction between the acid and MY721 already occurring during heating as has been observed in the homopolymerisation characterisation, but which cannot be determined in this case. Nonetheless, the reaction between

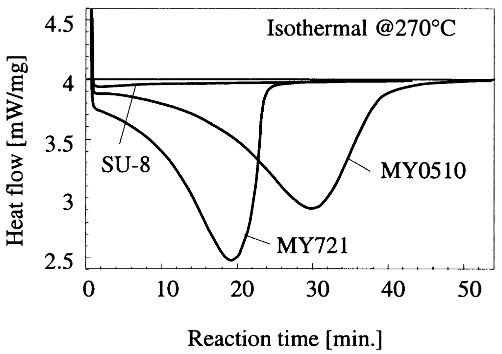

Fig. 3. Isothermal reaction peak of epoxy resin modifiers.

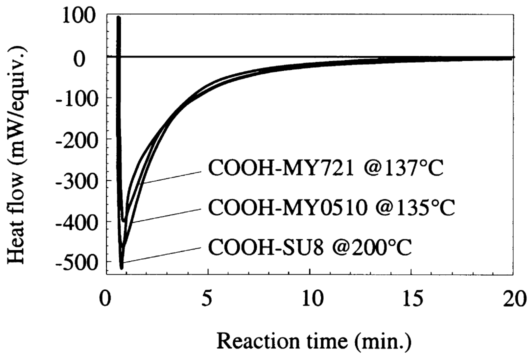

Fig. 4. Isothermal reaction peak of epoxy resins mixed with 4-ethylbenzoic acid.

the epoxy groups and carboxylic acid groups is shown to be efficient and fast whatever the structure of the epoxy molecule.

Mixing 2-(4-methoxyphenyl) ethanol with the epoxy resins does not show any reaction exotherm in temperature scans up to 220°C, at which temperature the alcohol volatilises. Although no reaction is observed at this temperature, the reaction should be chemically possible at a higher temperature. This result, nevertheless, shows that the reaction of epoxy with carboxyl groups, which initiated well below 220°C, is much more favourable.

To summarise, it has been shown that the homopolymerisation of epoxies in an extrusion process occurs before mixing is completed. However, in the short residence time typical of extrusion, such reaction remains limited, although it induces a slight increase in the average functionality per molecule. Furthermore, the reactivity between the COOH groups and epoxy groups has been emphasised and shown to be fast and effective, while the reaction between hydroxyl and epoxies appears less efficient. It can thus reasonably be assumed, as stated earlier, that during a reactive extrusion process the epoxy modifier will react primarily with the carboxyl PET chain ends. The resulting rheology is analysed below.

3.2. *Efficiency of epoxy modifiers with PET*

The influence of epoxy modifiers on the torque during mixing with PET in the Brabender rheometer is illustrated in Fig. 5. It is important to note that due to the exothermic reaction, and also because of viscous heating, the temperature of the melt increases by as much as 20°C after 10 min of mixing. The absolute torque values are thus not directly comparable since the experiments were not performed under strictly isothermal conditions. The results should thus be evaluated bearing in mind the evolution of the torque response as a function of the mixing time and the reaction efficiency. The unmodified PET only shows a torque decrease with time induced by degradation. This has been shown to occur in standard extrusion processes as well. Using well-controlled processing conditions, Gianotta et al. [20] showed that after a 2 min residence time at 260°C, a 10% drop of the weight-average molecular weight is obtained. With the SU-8 modifier, using a stoichiometric concentration (0.83 wt%), no reaction was observed with PET as the torque evolution was found to be identical to that of unmodified PET. To confirm this result, SU-8 was tested at a higher stoichiometric concentration (1.4 wt%), which again did not reveal any significant difference to virgin PET, as shown in Fig. 5. This clearly indicates that SU-8 has a negligible effect on the molecular chemistry of PET. When the MY0510 and MY721 modifiers are mixed at stoichiometric concentrations, an increase of the torque is clear. MY0510 shows a slow reaction with PET and the reaction is not complete after 20 min. MY721 presents the highest reactivity, illustrated by a fast initial increase of the torque with a first maximum in the torque value after approximately 8 min. This is followed by a stable stage during which a second reaction seems to occur. Since the carboxylic groups of the initial polymer are the main groups to react as was established in the preceding section, the first reaction rate corresponds to the branching of the PET structure where the multifunctional modifier reacts with at best *f* PET molecules. As the reaction proceeds, more epoxies are consumed by reaction with the COOH groups created by degradation reactions, epoxy homopolymerisation and by reaction with the PET hydroxyl groups. These different reactions lead to crosslinking. At the same time, unmodified PET shows a torque decrease induced by degradation. The overall torque evolution of the modified systems is thus strongly dependent on the reaction time because of the competing branching and degradation reactions. This results in the two maxima observed with 0.4 wt% of MY721. The higher reactivity of MY721 compared to MY0510 is not only due to a higher functionality, since solubility and catalysing effects of the environment most likely also play a role. In the modifier-model PET reactivity study, both modifiers showed similar reactivities. However, the COOH model molecule used was found to reduce the pH number of the environment, inducing catalysing effects [16], which could suppress the reactivity differences. Indeed, the homopolymerisation analyses carried out in the DSC cell have shown that MY721 is more reactive in a neutral environment, which is more representative of the PET melt to determine relative kinetics. It is worthwhile to note at this point that the structure of MY721 is the only one containing two trivalent nitrogens. This could also have a catalytic effect on the reactivity of the epoxy, since the nature of the adjacent groups are determinant for the relative reactivity [21].

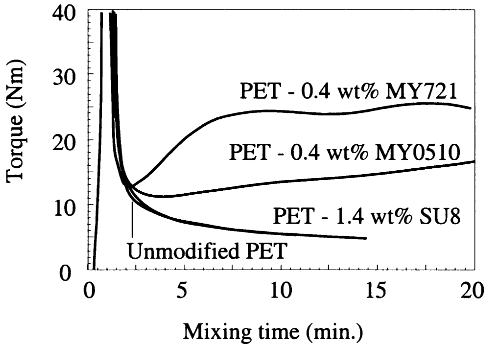

Fig. 5. Torque measurements carried out at 270°C for virgin PET, MY721 modified PET, MY0510 modified PET and SU-8 modified PET.

In the case of the MY721 modifier, a higher stoichiometric modifier fraction of 0.5 wt% and lower stoichiometric concentrations of 0.2 and 0.25 wt% were analysed in addition to the stoichiometric amount of 0.4 wt%. The corresponding torque responses are shown in Fig. 6, together with that of unmodified PET.

The stoichiometric amount of MY721 (0.4 wt%)

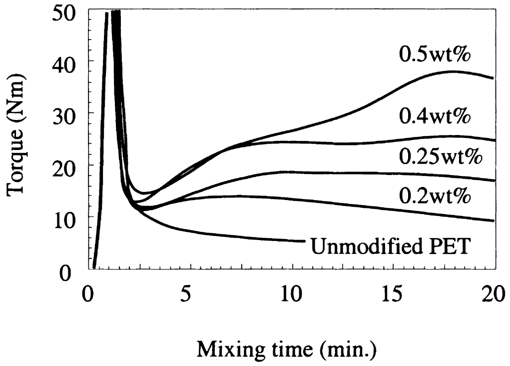

Fig. 6. Torque response of unmodified PET and modified PET at different concentrations of MY721.

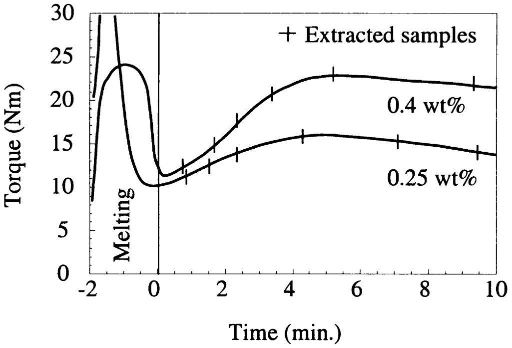

Fig. 7. Extraction of samples during the mixing process at concentrations of 0.25 and 0.4 wt% of MY721.

increases the torque of the virgin PET by a factor of 4.3 after 9 min of mixing. A second peak of similar height is observed after 17 min of mixing due to combined degradation and crosslinking processes as discussed previously. At a concentration of 0.5 wt%, the torque increase up to the first peak observed here at 8 min indicates that a similar amount of epoxy is reacting. After that, a marked deviation compared to the stoichiometric mixture is observed, and a strong second reaction with a maximum torque of 38 Nm occurs at 17 min of mixing. In this case, more secondary reactions are possible due to the excess of epoxy, which increases the probability of homopolymerisation, reactions with new carboxyl groups created by degradation and eventually with hydroxyl groups. Extensive branching and crosslinking consequently take place, which leads to a strong rigidification of the network. This is confirmed by the disappearance of the second peak at sub-stoichiometric concentrations. Both the 0.2 and 0.25 wt% concentrations increase the torque at a similar rate at short mixing times. From 4 min onwards, however, only 0.25 wt% of modifier allows to reach a higher branching factor sufficient to stabilise the modified material's torque response.

These results illustrate a clear transition in behaviour at 0.4 wt% of modifier, and further show that the calculated stoichiometric concentration (Eq. (1)) is appropriate in spite of the rather simple assumptions that were proposed.

In order to fully understand the reactions occurring during the Brabender reactive processing experiments, IV and COOH contents were analysed in samples extracted at several mixing times as shown in Fig. 7 for two MY721 modifier concentrations. The time scale has been shifted to the melting stage compared to the previous graphs to take into account only the reaction time.

The evolution of the IV and the COOH is shown in Figs. 8 and 9 as a function of reaction time with 0.25 and 0.4 wt% of modifier, respectively. For both concentrations, identical IV values are obtained at short mixing times with an initial IV value corresponding to the as-received unmodified PET. After 2 min of reaction, a difference in IV appears clearly. With 0.25 wt% of modifier, the IV increase then gradually levels off. An IV value of 1.037 dl/g is reached at the maximum torque previously determined at 270 s. Beyond this point, the IV stabilises at a maximum of 1.069 dl/g. With 0.4 wt% modifier, the IV increases strongly and the value corresponding to the maximum torque is 1.161 dl/g. These results show that with a modifier fraction as low as 0.25 wt%, an IV of over 1 dl/g can be attained but at the expense of a relatively long reaction time. With a higher modifier content, a higher IV can be obtained and shorter reaction times are required.

The COOH contents displayed in Fig. 9 show a large scatter in comparison to the IV results. However, the tendency observed demonstrates the participation of COOH groups in the reactivity between PET and the epoxy modifier. At 0.25 wt%, the COOH content is lowered from 15.3 for unmodified PET to 10.5 μmol/g. As expected, a lower value, 8.6 μmol/g, is obtained with 0.4 wt% of modifier. Inata et al. [22] obtained a minimum value of 5 μmol/g by using bis-2-oxazolines molecules added to a low molecular weight PET under a flow of nitrogen to minimise the PET degradation. In the present experiments, the increase of COOH content after 3 min of mixing is indicative of degradation. The static mixing without the use of nitrogen and the extraction of material during the experiment increase the degradation reaction in comparison to the conditions used by Inata et al. Nonetheless, in the early stage of mixing the results presented in Fig. 9 shows

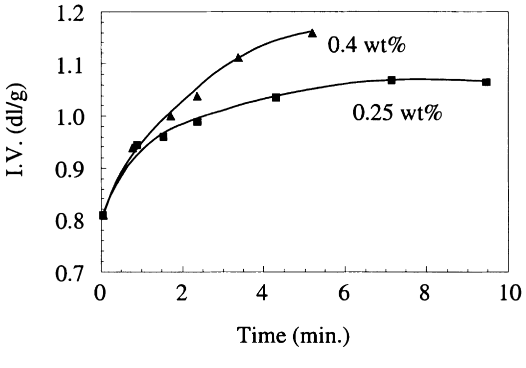

Fig. 8. Intrinsic viscosity (IV) measurements of extracted samples vs. reaction time.

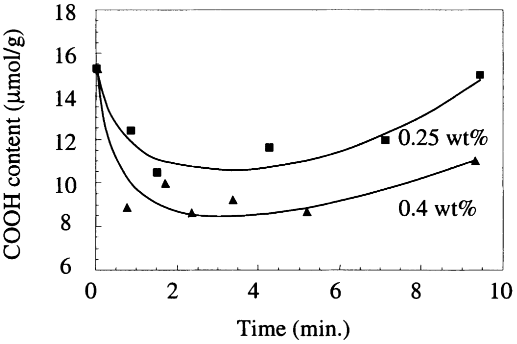

Fig. 9. COOH content of extracted samples vs. reaction time.

the efficiency of the reaction between the epoxy modifier and the COOH PET chain ends.

3.3. Reactive extrusion with tetra-functional epoxy

The efficiency of reactive extrusion was evaluated from the IV analysis of both extruded and Brabender mixed modified PET. Samples at stoichiometric concentrations were prepared by reactive extrusion with one and two successive extrusions. The second extrusion was performed to increase the reaction time. It should be noted that IV values are most sensitive to the middle class of the chain lengths [23], and that they are slightly underestimated for modified PET because, as illustrated by the GPC analysis in the next section, hydrodynamic volumes are smaller for branched polymers. The IV values obtained, of 0.789, 0.965 and 1.129 dl/g for unmodified PET extruded once, 0.4 wt% modified PET extruded once and 0.4 wt% modified PET extruded twice, respectively, show clearly the effect of subsequent extrusions. For 0.4 wt% modified PET extruded once, the IV value of 0.965 dl/g corresponds to a reaction time in the Brabender rheometer of 1 min (Fig. 8) after the melting stage that lasted 160 s. During extrusion, the total residence time was measured to be 40 s including the melting stage. The ratio between the total Brabender and extruder processing times, of about 5, simply indicates a better shearing and mixing efficiency and that less degradation occurs in the latter. The same time ratio of 5 is obtained when comparing the IV values of 1.129 dl/g obtained after the second extrusion, as well as after 160 s of melting and 230 s of reactive mixing in the Brabender rheometer.

For the processing conditions studied, a good time correlation is found between the reactive extrusion and the Brabender rheometer experiments. The latter are thus considered to be representative of an extrusion process at least at shorter times before extensive degradation occurs. They are therefore considered to be an appropriate tool for optimising the reactive extrusion process.

3.4. Molecular architecture analysis

The foamability of a material is to a large extent controlled by its structural characteristics, which determine the rheological behaviour of the melt. The main structural parameters of extruded modified PET have been studied using GPC experiments.

The MWD is plotted as the differential weight polymer fraction [10] as a function of log (*M*) in Fig. 10. This representation, commonly called differential log (MWD), is suitable for comparing different materials.

The difference between the unmodified PET and the 0.4 wt% MY721 modified PET extruded once (PET-0.4 wt%_1) appears to be small and only a small portion of higher masses is obtained. A remarkable increase of high masses is obtained after the second extrusion, which increases the reaction time and produces a longer tail towards high masses.

Number-, viscosity-,weight- and *z*-average molecular weights as well as the IV values are summarised in Table 2 for unmodified PET extruded once (Unmodified PET#1), 0.4 wt% MY721 modified PET extruded once (PET-0.4 wt%_1) and 0.4 wt% MY721 modified PET extruded twice (PET-0.4 wt%_2).

M_n is calculated from the polydispersity factor and the measured M_w. The value of unmodified PET is higher than the value given by Eastman (26,000 g/mol), which would indicate that the calculation of M_n is overestimated. Fig. 11 shows all characteristic molecular weights normalised to a value of 1 for the unmodified PET. The *z*-average molecular weight (M_z) of a polymer highlights the content of high masses and indeed shows the largest increase for the modified systems compared to unmodified PET. This growth in M_z becomes particularly significant with an eight-fold increase after the second extrusion of the 0.4 wt% epoxy-modified PET. The polydispersity factor also indicates a broadening of the MWD for the twice extruded material. Furthermore, it should be emphasised that very high molecular weights (higher than 3×10^6 g/mol) are obtained. These results demonstrate the chain extension efficiency of the modifier whose beneficial influence on the rheological characteristics of the material was already pointed out previously. The latter, however, is

Table 2
Characteristic molecular weights obtained by GPC and intrinsic viscosity (IV) measurements of extruded samples

Polymer	M_n	M_v	M_w	M_z	Polydispersity	IV (dl/g)
Unmodified PET#1	31,300	53,500	57,200	86,500	1.83	0.789
PET-0.4wt%_1	35,900	61,200	66,000	114,200	1.84	0.965
PET-0.4wt%_2	36,400	103,300	109,300	687,600	3.00	1.129

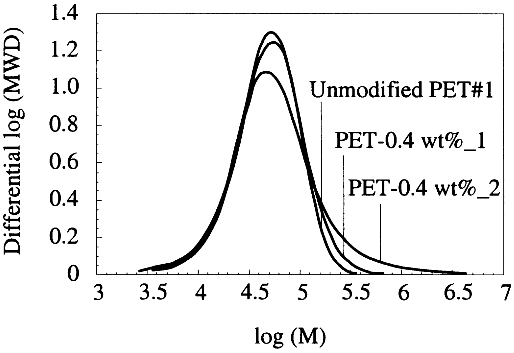

Fig. 10. Comparison of the differential log (MWD) vs. log (M) for unmodified PET 9921#1, 0.4% epoxy-modified PET extruded once, 0.4% epoxy-modified PET extruded twice.

also influenced by the branching efficiency. To investigate the branching efficiency, the hydrodynamic volumes of the molecules are taken into account. A branched molecule in solution has a smaller hydrodynamic volume than a linear molecule of the same molecular weight. Whereas linear chains exhibit the classical Mark–Houwink–Sakurada law behaviour of viscosity increase with M_w [24], the branched polymers show a slower increase [25]. Long chain branching is characterised by means of a branching factor g' defined as [26]:

$$g' = \left(\frac{[\eta]_b}{[\eta]_l}\right)_M = g^k \tag{2}$$

where the b and l indices represent branched and linear molecules, respectively. The corresponding viscosities, $[\eta]$, correspond to equivalent masses. The branching factor g is the ratio of the mean square radius of gyration of the same species, and k is the branching structure factor. The Universal Calibration states that, at equal elution volume, the molecular weight of linear (M_l) and branched species (M_b) of the same polymer are related by:

$$[\eta]_b M_b = [\eta]_l M_l \tag{3}$$

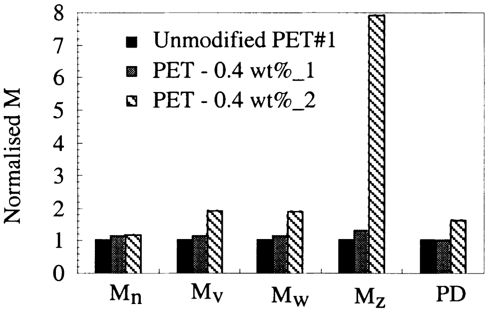

Fig. 11. Normalised values of M_n, M_v, M_w, M_z and polydispersity for three polymers, unmodified PET#1, 0.4 wt% epoxy-modified PET extruded once (PET-0.4 wt%_1), 0.4 wt% epoxy-modified PET extruded twice (PET-0.4 wt%_2).

This mass correction, allowing M_b to be calculated, is used in the determination of g'.

The results of GPC analyses, reported in Fig. 12 as $\log(\eta)$ vs. $\log(M)$, strictly obey the Mark–Houwink relationship for the linear structure of unmodified PET. A linear mean square regression yields a value of 0.713 and of 2.79×10^{-2} for the α and K Mark–Houwink parameters, respectively.

As the nature of the polymer is the same for unmodified and modified PET, the linearity between $\log(\eta)$ and $\log(M)$ should be respected if the modified structure was formed by linear chains. This is, however, not observed for the once extruded 0.4 wt% sample, where a deviation from linearity corresponding to the presence of branched molecules is evident for masses higher than 100,000 g/mol. For the twice extruded 0.4 wt% sample, an even more pronounced deviation from the Mark–Houwink relationship is observed over the entire range of molecular weights.

In the low molecular weight range, the curve shows a non-linearity with a reduction of the viscosity. It would, on the contrary, be expected that the viscosity increases for branched low molecular weight structures when compared to linear macromolecules. The observation of a viscosity drop in the present study is attributed to a deviation from the universal calibration curve resulting in slightly overestimated molecular weights in this range. For large masses, the strong deviation from the Mark–Houwink law confirms the presence of branching with a related lowering in viscosity due to a reduction of the molecular hydrodynamic volumes. Neglecting the small masses due to the uncertainty of the results, Eq. (2) is plotted in Fig. 13 using the results presented in Fig. 12 to obtain the g' factor. During the first extrusion of modified PET, the branching factor reaches a minimum value of 0.7 at the highest masses obtained of 8×10^5 g/mol. During the second extrusion, further branching occurs and g' reaches a value lower than 0.2 for the very high masses above 3×10^6 g/mol. This low value of g' is similar to the results of Lecacheux et al. who studied branched low-density polyethylene (LDPE) [25].

To determine the number of branches per macromolecule,

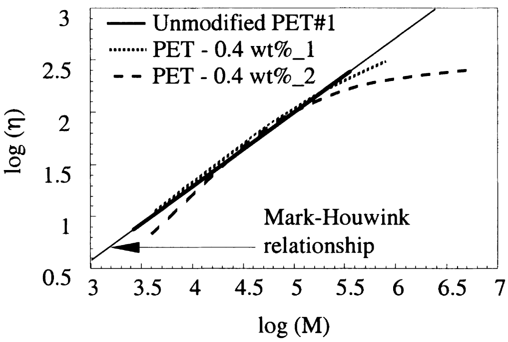

Fig. 12. Relationship between log (η) and log (M) for unmodified PET#1, 0.4 wt% epoxy-modified PET extruded once, and 0.4 wt% epoxy-modified PET extruded twice.

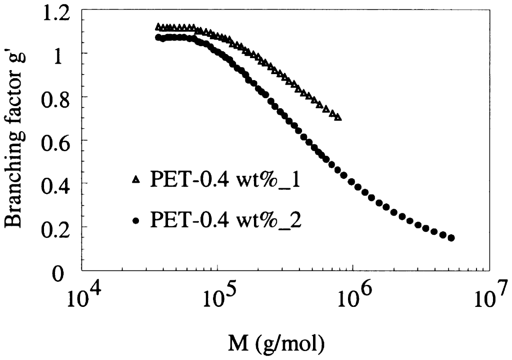

Fig. 13. The g' branching factor calculated using Eq. (4) for both modified materials as a function of the molecular weight (M).

the Zimm–Stockmayer semi-empirical model of tri-functional branching and polydisperse polymers, was chosen [11]:

$$g'^{1/k} = \frac{6}{n}\left\{\frac{1}{2}\left(\frac{2+n}{n}\right)^{1/2}\ln\left[\frac{(2+n)^{1/2}+n^{1/2}}{(2+n)^{1/2}-n^{1/2}}\right]-1\right\} \quad (4)$$

where n is the weight average number of branch points per molecule. The real functionality of MY721 is 3.78, but the above equation is considered as most representative of the real structure obtained. It is indeed not expected that a full conversion of the epoxy modifier is achieved at the end of the extrusion process. The branching structure parameter, k, (Eq. (2)) is in theory equal to 0.5 for star-branched polymers and 1.5 for comb-like branched polymers [25]. Owing to a lack of studies on branched PET, k is assumed to be equal to 0.8 which, according to Glöckner [11], is the most representative value for an undefined branched structure.

Eq. (4) yields a branch number, n, for the modified PET sample extruded twice, illustrated in Fig. 14 as a function of M. The same figure also illustrates the average mass between branch points M_{bp}, which can be calculated as:

$$M_{\mathrm{bp}} = \frac{M}{[n(f-1)+1]} \quad (5)$$

where f is the functionality.

The branch number n increases strongly above 1×10^6 g/mol masses, reaching a maximum value of 109 branches per molecule. At this point, M_{bp} approaches an asymptotic value of 24,000 g/mol. This asymptotic value is interestingly close to the M_{n} value of 26,000 g/mol given by the material supplier for the original polymer. M_{bp} is indeed expected to be equal to M_{n} since this corresponds to the average chain length from which an extended chain can be built. Fig. 10 shows that only a small portion of the MWD corresponds to the highly branched structures with molecular weights above 10^6 g/mol. However, it is well established that even a small quantity of these branched large masses greatly change the rheological behaviour of the polymer [27]. The study of the extensional viscosity of these modified polymers will be described in a future publication.

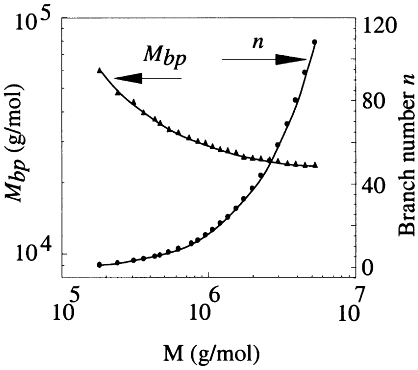

Fig. 14. Representation of the branch number, n, and the average molecular mass between branch points, M_{bp}, as a function of M for 0.4 wt% modified PET extruded twice

4. Conclusions

The improvement of the extensional viscosity of PET requires an increase in the molecular mass. For this purpose, reactive extrusion coupled to the use of tri-, tetra- and octo-functional epoxy modifiers has been studied. Reactivity analyses and structural characterisations lead to the following conclusions:

1. The reactivity study has shown that the homopolymerisation of tri- and tetra-functional epoxies in an extrusion process occurs before mixing is completed. However, in the short residence times typical of extrusion, such a reaction remains limited. It nevertheless induces a slight increase in the average functionality per molecule. By using model molecules, the reactivity between COOH and epoxy groups has been emphasised and shown to be fast and effective, while the reaction between hydroxyl and epoxies appears less efficient. It seems thus reasonable to assume that during a reactive extrusion process the epoxy modifier will react primarily with the carboxyl PET chain ends.
2. The epoxy resins showed considerable differences in their reactivity with PET. No reaction between PET and the octo-functional epoxy modifier was observed, both at stoichiometric and at higher stoichiometric concentrations. This clearly indicates that this epoxy resin did not affect the molecular architecture of PET. A stoichiometric concentration of the tri-functional epoxy has been shown to react with PET at a slow rate, which makes its use in the extrusion process difficult.
3. The use of the tetra-functional epoxy resin has been shown to increase strongly and efficiently the rheological properties of PET.
    - Experiments confirm that a concentration of 0.4 wt% of the tetra-functional epoxy corresponds to the stoichiometric concentration for the PET used. At this concentration, calculated according to the initial M_{n} of the PET, a transition in the structural build-up during reactive extrusion was observed.

- The epoxy–COOH reaction has been shown to occur readily during reactive extrusion, leading to a lowering of the COOH content.
- A minimum reactive extrusion time is required to reach a complete reaction, as indicated by the IV analysis. In the present work, this time corresponds to two extrusions in the laboratory twin-screw extruder used. This residence time is suitable for most commonly used extruders in industrial processes.
- With a complete reaction, an eight-fold increase of M_z is obtained as shown by GPC analysis. Branching of PET occurs due to the multifunctionality of the epoxy resin. The branching factor g' allows to estimate the branch number n and the average mass between branch points M_{bp} as a function of M. For high masses above 10^6 g/mol, n strongly increases and M_{bp} was decreased to a plateau value of 24,000 g/mol corresponding to the number-average molecular weight of the original polymer.

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