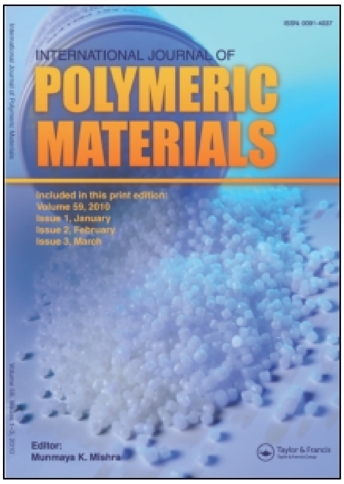

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Influence of the polyethyleneglycol content on the properties of ethyleneglycolterephthalate/polyethyleneglycol terephthalate copolymers

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INFLUENCE OF THE POLYETHYLENEGLYCOL CONTENT ON THE PROPERTIES OF ETHYLENEGLYCOLTEREPHTHALATE/ POLYETHYLENEGLYCOL TEREPHTHALATE COPOLYMERS

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The effect of the polyethyleneglycol (PEG) content on the properties of the ethyleneglycol terephthalate (EGT)/polyethyleneglycol terephthalate (PEGT) copolymers has been studied. The PEG content varied over a wide range (5–70% PEG). To obtain information on the solubility and on the thermal properties, the following methods: turbidimetry, differential scanning calorimetry (DSC), thermogravimetry and differential thermogravimetry (TG, DTG) have been used. The turbidimetric characteristics are dependent on composition copolymers. The incorporation of increasing amount of PEG 4000 in EGT/PEGT copolymers has a pronounced effect on the properties: increases viscosity and solubility of copolymers, decreased glass transition, cold crystallization and melting temperatures and also decreased crystallization and melting heat. These changes are desirable for better processing of these copolymers comparatively with PET in products with higher elasticity and hydrophilicity. It must be take into account, however, that above 20 wt% PEG the copolymers the thermal stability is significantly affected.

Keywords: ethyleneglycol terephthalate/polyethyleneglycol terephthalate copolymer, turbidimetry, differential scanning calorimetry, thermogravimetry

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1. INTRODUCTION

The ethyleneglycol terephthalate/polyethyleneglycol terephthalate copolymers were studied mainly to establish the effect of the diethyleneglycol (DEG) content on the properties of the polyethylene terephthalate (PET) because of the DEG formation during the industrial synthesis of PET so that DEG units are always incorporated in polymer chain [1]. It has been established that all transition temperatures decrease with increasing DEG content [2, 3]. The crystallinity degree and rate of crystallization are significantly affected because DEGT units are predominantly concentrated in the amorphous regions of partially crystalline polymer [4].

The copolyesters also offer a compromise between material cost and properties, being also especially suitable for reprocessing of some used products such as bottles, by injection-molding technology [5]. Only a few studies dealt with EGT/PEGT copolymers [6] mainly focused on the hydrophilicity increase by PEG incorporation.

The present paper is intended to furnish information on the solubility and thermal properties of several copolymers EGT/PEGT with a wide range of PEGT content that offer some improved properties for textile applications in respect to PET.

2. EXPERIMENTAL

2.1. Materials

The EGT/PEGT copolymers were supplied by S. C. FIBRESIN S. A. Iasi. They were obtained by bulk copolymerization of terephthalic acid with polyethyleneglycol 4000 (PEG 4000) and EG in presence of calcium acetate/Sb_2O_3 as a catalytic system.

Some characteristics of studied samples are given in Table 1.

The dependence of the intrinsic viscosity on PEG content–Figure 1–indicates that up to 12 wt% PEG, the viscosity of EGT/PEGT copolymers is very close to that of PET. A sudden in crease appears for 15–30 wt% PEG, then the values are approximately constant for a wide range of 30–70 wt% PEG content. Therefore in the discussion of the variation of other properties of copolymers, one must consider both the effect of PEG content and intrinsic viscosity (respectively molecular weight) change as it appears in Figure 1.

TABLE 1 Characteristics of the Studied EGT/PEGT copolymers

No.	PEG in polycondensation feed (%)	$[\eta]^*$ (dL/g)
1	0	0.725
2	5	0.637
3	7	0.723
4	10	0.724
5	12	0.773
6	15	0.840
7	21	0.940
8	25	1.080
9	30	1.160
10	40	1.150
11	50	1.110
12	70	1.150

*Ubelhode viscometer, 25 ± 0.2°C; solvent: phenol/tetrachloroethane (3 vol/1 vol); concentration 0.5–0.2 g/dL.

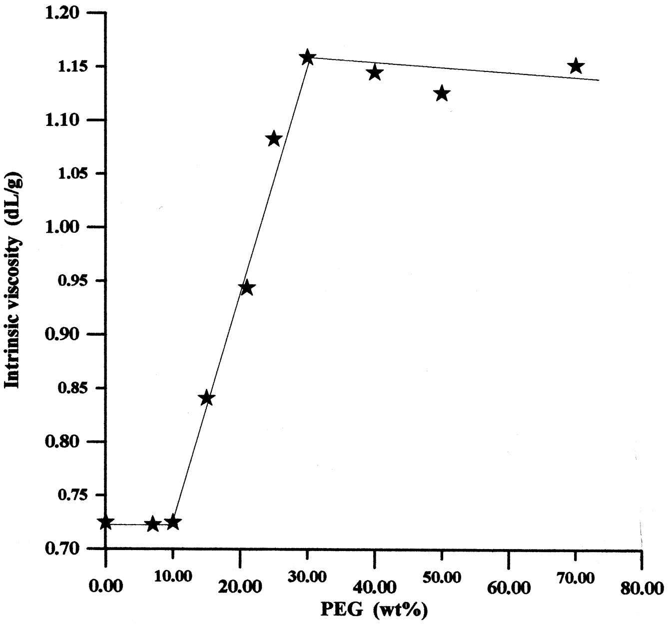

FIGURE 1 Dependence of the intrinsic viscosity on PEG content of EGT/PEGT copolymers.

2.2. Investigation Methods

The investigation methods employed in the present study were turbidimetry, differential scanning calorimetry (DSC), thermogravimetry (TG) and differential thermogravimetry (DTG).

The turbidimetric titration has been performed on laboratory-made installation [7] in the following conditions: solvent phenol/tetrachloroethane (3 vol/1 vol), solution concentration 0.03 g/dL, non-solvent *n*-heptane/carbon tetrachloride (9 vol/1 vol), temperature 25 ± 2°C, the flow rate of non-solvent 0.388 mL/min, under vigorous stirring.

Calorimetric measurements were done on 10–15 mg powdered samples by means of a Mettler DSC 12E instrument. The instrument was calibrated daily using indium as reference. All scans were conducted under a nitrogen atmosphere 30 mL/min, temperature range −40–400°C, heating rate 10°C/min. The heat of fusion or of "cold" crystallization was determined by comparing the peak area to that of a known weight of the reference material (indium) whose melting heat is $\Delta H = 28.43$ J/g.

The TG/DTG curves were recorded on a Paulik-Paulik-Erdey derivatograph from MOM — Budapest, powder samples of 50 mg, heating rate 12°C/min, air flow 30 mL/min.

3. RESULTS AND DISCUSSION

3.1. Turbidimetric Titration Results

The turbidimetric titration curve shape and its characteristics such as: volume of non-solvent required for the beginning of precipitation (V_0); total volume of non-solvent for precipitation of entire polymer quantity ($V_{\max}$), the difference ($V_{\max}-V_0$), maximum optical density ($D_{\max}$), optical density corresponding to the precipitation of a half of polymer ($D_{1/2}$) and slope of the turbidimetric curve $dD/d\gamma$ give informations on the solubility, average molecular weight and molecular weight distribution of the samples [8–12].

In the case of copolymers, all these characteristics are also dependent on composition and comonomer distribution [13].

In Figure 2 are presented the normalized turbidimetric curves of the PET and EGT/PEGT copolymers with various PEG content in coordinates $(1-D_t/D_{\max})-(1-\gamma)$, where each value of the optical density namely, optical density at "*t*" moment of precipitation (D_t) and maximum optical density ($D_{\max}$) were reported in terms of $(1-\gamma)$ where $\gamma = V_{ns}/V_{ns}+V_s$, is the volume fraction of non-solvent. This normalization procedure corrects the dilution effects. It can be easily

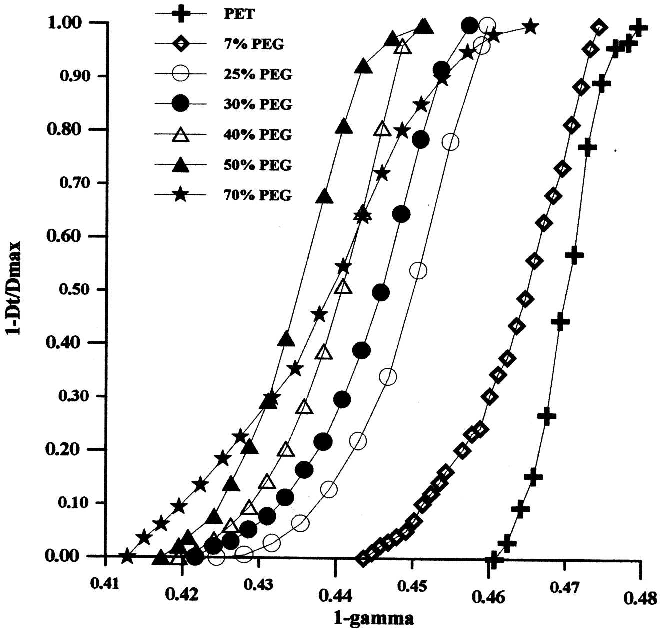

FIGURE 2 Normalized turbidimetric titration curves of the PET and EGT/PEGT copolymers with various PEG content.

remarked that the EGT/PEGT curves are shifted to lower values of $(1-\gamma)$ with increasing PEG content, therefore a higher quantity of nonsolvent is necessary to precipitate the copolymers with increased PEG content, as it clearly apparent in Figure 3. In other words the solubility of copolyesters increases with PEG content.

The turbidimetric titration curve of PET exhibits a high slope, while for EGT/PEGT copolymers the slope decreases together with the nonhomogeneity or polydispersity of samples; the lowest slope exhibits the curve corresponding to copolymer with 70% PEG, that has probably a high compositional and molecular weight polydispersity. The slopes of the curves of copolymers with 25–50% PEG have almost the same values. The increase of the amount of low molecular weight fraction with increasing PEG content is also clearly observed.

Considering the variation $[\eta]$–PEG content from Figure 1 and dependence of V_0, $V_{\max}$, $V_{\max}-V_0$ on copolymer composition from Figure 4, it seems that the turbidimetric titration is mainly influenced by difference in copolymer composition. The increase of the nonsolvent volume with PEG content appears in the 5–30% PEG

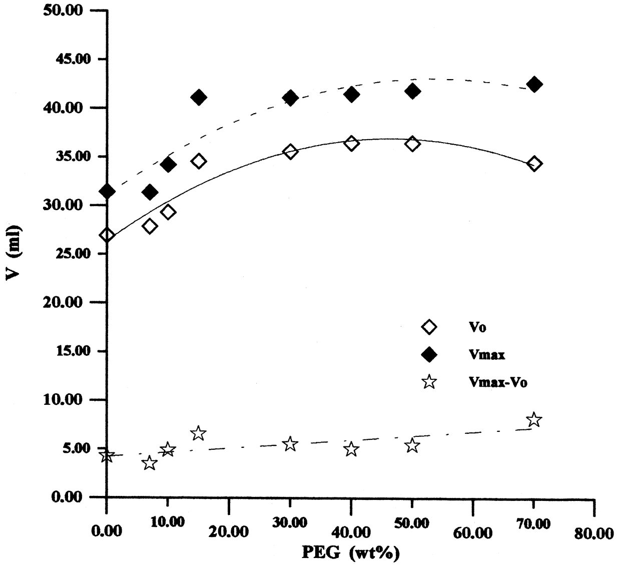

FIGURE 3 Variation of V_0, $V_{\max}$, and $V_{\max}-V_0$ with PEG content of the EGT/PEGT copolymers.

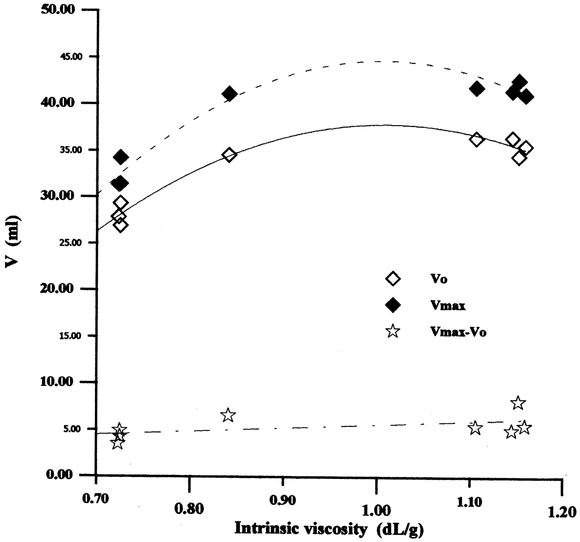

FIGURE 4 Variation of V_0, $V_{\max}$, and $V_{\max}-V_0$ with the intrinsic viscosity of the EGT/PEGT copolymers.

composition range, then almost the same quantity of non-solvent is required for precipitation of all other copolymers, therefore the copolymers have similar solubilities in the phenol/tetrachloroethane-*n*-heptane/CCl_4 solvent/non-solvent system.

Variation of $D_{1/2}$ and $D_{\max}$ with PEG content and intrinsic viscosity are presented in Figures 5 and 6, respectively.

The dependence on PEG content of both values is similar: a curve with a maximum at 25% PEG. The maximum could be due to the formation of smaller particles in solution of copolymers containing 10–30% wt PEG in respect to other solutions, considering that all experimental conditions were similar.

These values mainly linearly depend on the concentration of solutions and on viscosity as it was shown with other samples, too [10–12].

3.2. DSC Results

The DSC results are presented in Figure 7 and Table 2. The DSC curves of EGT/PEGT copolymers with a PEG content up to 20 wt% have a shape similar to that of PET, exhibiting three transition regions in −40–250°C interval, namely: glass transition (*Tg*), "cold" crystallization (*Tcr*) and melting (*Tm*), with characteristic temperatures and transformation heats given in Table 2.

The DSC curves of the copolymers with a PEG content higher than 20 wt% exhibit only a large "cold" crystallization peak overlapped with

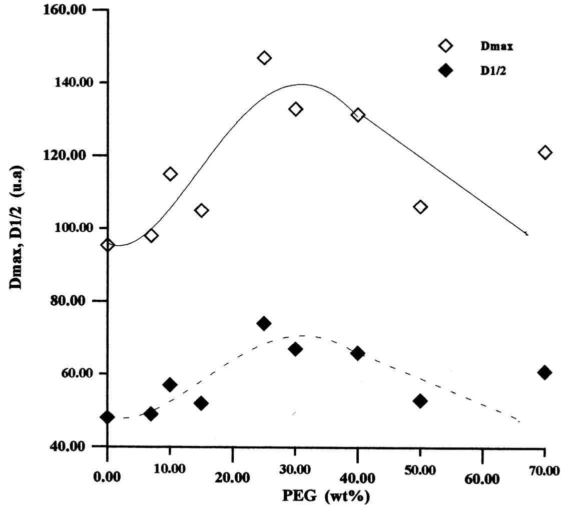

FIGURE 5 The dependence of $D_{1/2}$ and $D_{\max}$ on PEG content.

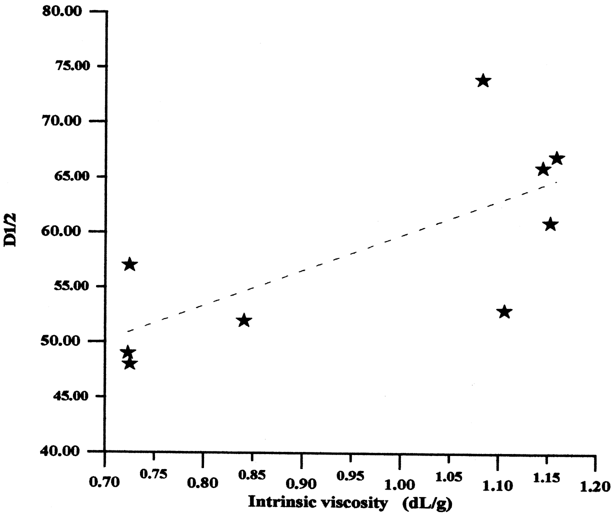

FIGURE 6 The dependence of $D_{1/2}$ and D_{max} on intrinsic viscosity.

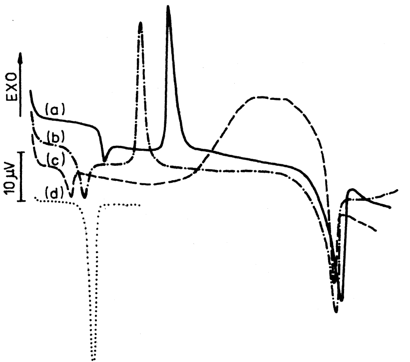

FIGURE 7 DSC curves of PET (a), EGT/10 wt% PEGT (b), EGT/40 wt% PEGT (c), copolymers and PEG (d).

melting peak. The endothermic process occurring around 50°C was assigned to the melting of PEG microdomains as it appears in DSC curve of PEG of Figure 7 and also on the curves of Figure 8 recorded for EGT/PEGT copolymers with 40 and 60 wt% PEG –Figure 8a–, because they clearly appear both by heating or cooling mode–

TABLE 2 The DSC Results for EGT/PEGT copolymers

No.	Content PEG in copolymer (wt%)	*Tg* (°C)	*Tcr* (°C)	Tm (°C)	Δ*Hcr* (J/g)	Δ*Hm* (J/g)
1	0	76	125	246	28.5	34.9
2	5	68	118	242	28.3	34.8
3	7	58	113	240	28.1	34.9
4	10	52	101	242	25.4	34.7
5	12.5	50	95	229	26.6	27.8

Δ*H*crist. and Δ*Hm* are the "cold" crystallization heat and respectively melting heat.

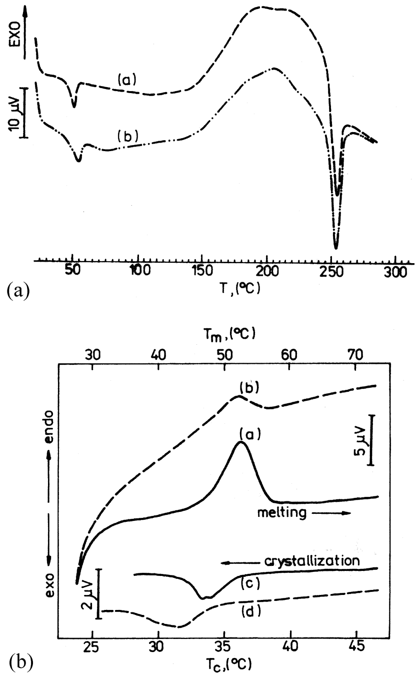

FIGURE 8 DSC curves of EGT/40 wt% PEGT (a) and EGT/60 wt% PEGT (b) copolymers recorded by heating and cooling mode.

Figure 8b. The crystallization takes place at lower temperature increasing PEG content.

All transition temperatures and heats decrease with increasing PEG content. This means an increase of the flexibility of chains and the amorphous phase content by copolymerization. The variation is an

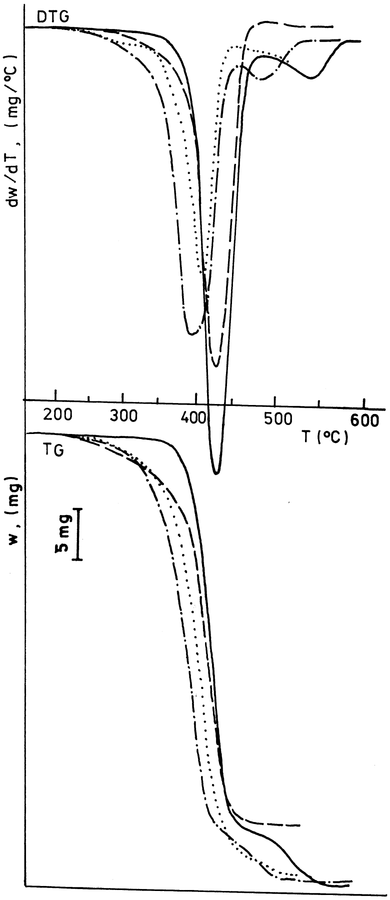

FIGURE 9 TG/DTG curves of PET (—), PEG (......), 90 wt% EGT/10 wt% PEGT (- - -) and 60 wt% EGT/40 PEGT(-.-.-.).

expected one considering the low glass transition temperature of PEG of −37°C (or −59°C), given in literature [14, 15] and according to calculated values using the Flory-Fox relationship [16].

The crystallinity reduction could have advantages in processing of polyester-based products.

3.3. Thermogravimetric Results

Both TG and DTG curves of the copolymers are shifted toward lower temperatures with respect to that of PET. With increasing PEG content of copolymers –Figure 9–, all thermogravimetric characteristics

TABLE 3 Thermogravimetric Results for PET, PEG, and EGT/PEGT Copolymers

	Characteristic temperatures						
Samples	*Ti* (°C)	*Tm* (°C)	*Tf* (°C)	ΔW (%)	E_{SM} (kJ/mol)	n_{SM}	$\ln A_{SM}$
PET	320	420	465	87.2	240.5	1.2	41.7
15% PEG	330	415	458	84.3	157.4	0.8	26.6
21% PEG	328	412	452	80.0	183.5	1.2	31.9
40% PEG	295	402	460	86.0	163.3	1.0	28.6
50% PEG	240	395	460	85.5	132.6	0.9	22.8
PEG	328	410	450	87.0	198.5	1.3	33.1

T_I, T_m, T_f—onset, maximum weight loss rate (peak temperature) and respectively at the end of process temperatures; ΔW—weight loss; E_{SM}, A_{SM}, n—overall activation energy, pre-exponential factor and reaction order evaluated by Swaminathan-Madhavan method [17].

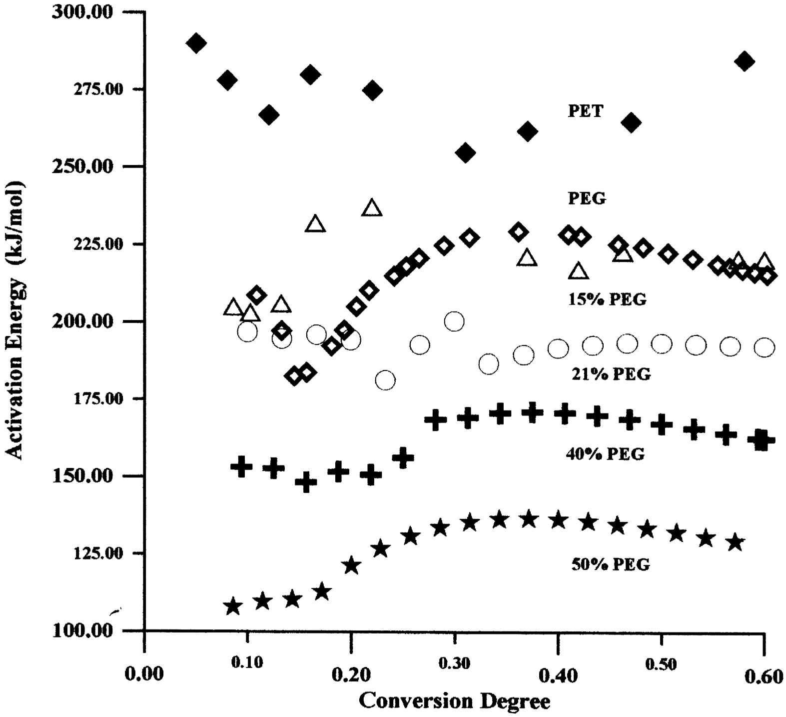

FIGURE 10 Dependence of activation energy evaluated by Reich-Levi method [18] *versus* conversion degree.

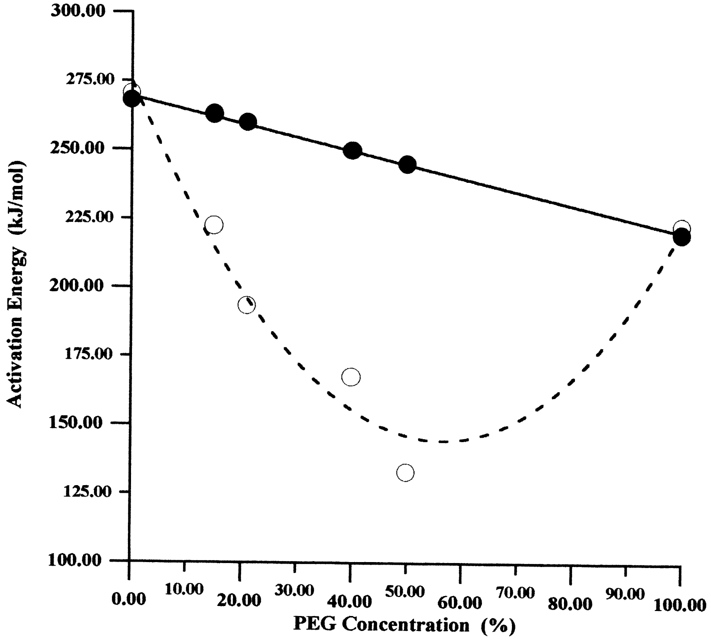

FIGURE 11 The dependence of the average activation energy for conversion degree interval $\alpha = 0.2 - 0.6$ *versus* PEG content of EGT/PEGT copolyester (o)-evaluated and (•)–calculated value as weight average.

take lower values –Table 3–, therefore the copolymers have a decreased thermal stability.

The curves of dependence of the activation energy on degradation degree of copolymers all lie below that of PET and the values are almost constant for all samples in the 0–0.6 conversion degree range, –Figure 10. There is a large difference between the average activation energy of decomposition of copolymers and the corresponding values evaluated as weight percentage from those of components, –Figure 11. This difference could be explained by new chemical structure obtained by copolymerization and that the block are not segregated in micro-domains with individual behaviour.

The dependence of all thermogravimetric data and overall kinetic parameters on copolyester composition lead to the conclusion that their thermal stability is significantly decreased. It is maintained at satisfactory values for a PEG content only up to 20 wt%.

4. CONCLUSION

The incorporation of increasing amount of PEG 4000 in EGT/PEGT copolymers has a pronounced effect on the properties by increased viscosity and solubility of the copolymers, decreased glass transition, "cold" crystallization and melting temperatures and also decreased crystallization and melting heat.

These changes are indicative of better processing of these copolymers as compared with PET in products with higher elasticity, hydrophilicity and dyeability.

However it should be taken into account that the copolymers are less thermally stable than PET when optimal conditions for processing or reprocessing are to be established.

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