

Influencing the Crystallization Behavior of PET-Based Segmented Copoly(ether Ester)

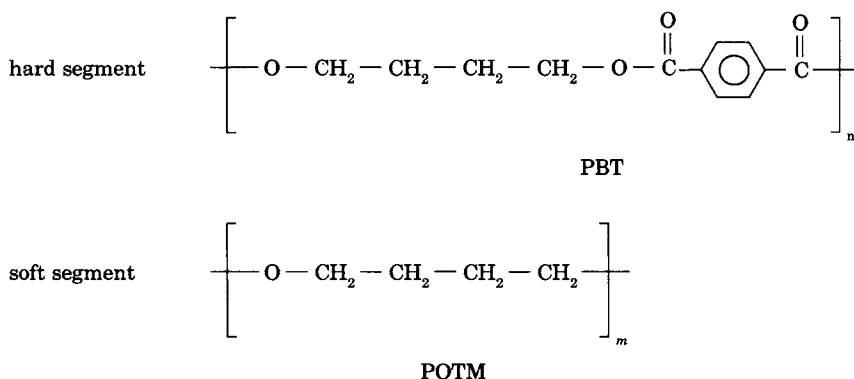
J. J. ZEILSTRA, *Enka Research Institute Arnhem, Velperweg 76, 6824 BM Arnhem, The Netherlands*

Synopsis

Segmented copoly(ether ester) based on poly(ethylene terephthalate) and poly(oxytetramethylene) suffers from having a rather low rate of crystallization. The crystallization behavior of this elastomer can be influenced by cocondensation of selected diols and addition of nucleating agents and plasticizers. Changes of the crystallinity and morphology are studied by differential scanning calorimetry and dynamic-mechanical analysis, respectively. Mechanical properties in relation to the different crystallinities obtained are reported.

INTRODUCTION

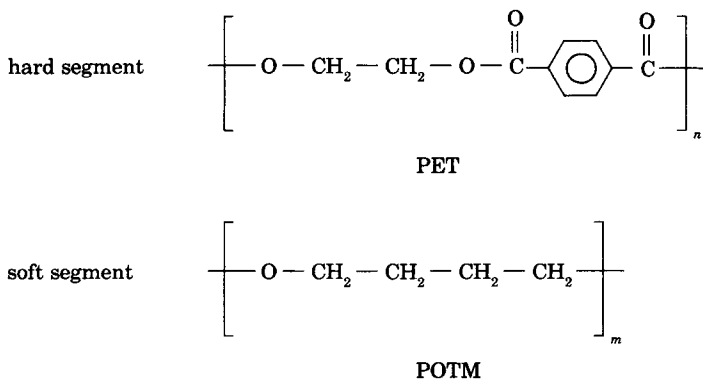
Block copoly(ether ester)s have been studied both for academic interest and for industrial application. These polymers belong to the engineering plastics and are commonly referred to as thermoplastic polyester elastomers, because of their elastomeric properties which are combined with the processability of thermoplastics. The polyether and polyester chain segments prove to segregate into separate phases in the solid state. The polyether segments, commonly referred to as the "soft" segments, form at ambient temperature a liquidlike phase due to their low glass-transition temperature and low melting point, whereas the polyester segments, the "hard" segments, usually crystallize, thus providing dimensional stability and minimizing cold flow. The morphology of these block copoly(ether ester)s has been studied extensively by several groups.^{1,2} A typical representative of these elastomers is the copoly(ether ester) based on poly(butylene terephthalate) (PBT) and poly(oxytetramethylene) (POTM) segments.



Physical properties such as modulus, creep resistance, compression set and solubility are highly dependent on the ester-segment structure, its

concentration and on the state of crystallization.³⁻⁷ Failure properties such as tensile strength, tear strength, abrasion resistance, etc., depend to a larger extent on the morphology. Consequently, the amorphous phase composition is also of importance. Low temperature flexibility and impact resistance reflect the glass-transition temperature(s) of the amorphous phase and the melting point of the soft segment material.

The crystallization rates of such copolymers reflect those of the polyester homopolymers. For example, the PBT-based copolymer shows a high crystallization rate, whereas the poly(ethylene terephthalate) (PET)-based copolymer suffers from a rather low rate of crystallization.^{4-6,8} The mechanical properties of the latter strongly depend on molding conditions as well as on heat history after the molding operation.



In fact, the unmodified PET-based elastomer is unsuitable for most injection-molding applications because of its low rate of crystallization and high mold temperature requirements. Inadequate mold temperature results in significant dimensional changes or deformation owing to post-crystallization in parts that experience an in-service heat history. Consequently, modification is necessary to encourage nucleation and sufficient chain mobility in order to crystallize at a relatively high rate.

As part of our continuing efforts to enhance our understanding of block copoly(ether ester)s and block copoly(ester ester)s,⁸⁻¹¹ we have continued our study of the PET-POTM block copolymer. The objective of our study was, first, to modify the elastomer in order to influence its crystallization rate and, second, to determine changes in dynamic-mechanical properties in relation to the different crystallinities obtained after injection molding. Consequently, first of all, an inventory of measures to modify this elastomer is required.

Compared with the PET homopolymer, polyether-modified PET already shows a higher crystallization rate¹²⁻¹⁴ and a lower glass-transition temperature,⁸ indicating an enhanced chain mobility. Other factors influencing the crystallization behavior in a positive way, can be derived from the crystallization kinetic theory.¹⁵ From this theory it follows that the spherulite growth rate ν can be described with the following equation:

$$\nu = \nu_0 \exp\left(\frac{-E_D}{RT}\right) \exp\left[\frac{-CT_m^0}{T(T_m^0 - T)}\right]$$

where ν_0 is a universal constant for semicrystalline polymers, $\nu_0 \sim 7.5 \times 10^8 \mu\text{m/s}$. At low to moderate molecular weights, however, the value of ν_0 is dependent on the molecular weight; its value increases with decreasing molecular weight due to increased molecular mobility. E_D is an activation energy for transport, which depends on the glass-transition temperature (T_g). T_m^0 is an "effective" melting point, T is the temperature of the sample (K), C is a constant with the value ~ 265 K, and R is the gas constant. According to this equation, several parameters may be affected.

Influence of Molecular Weight (\overline{M}_n)

The spherulite growth rate and the half-time of crystallization of the PET homopolymer have been shown^{16,17} to be strongly dependent on \overline{M}_n , i.e., a lower \overline{M}_n results in an enhanced ν . Taking this into account, the obvious choice would be to use a PET-POTM block copolymer with low \overline{M}_n in order to obtain an acceptable crystallization behavior. However, we are not completely free to choose \overline{M}_n : a low \overline{M}_n results in a low melt viscosity, which may have a negative influence on the moldability; the required mechanical properties cannot be obtained with (too) low an \overline{M}_n .

Influence of Glass-Transition Temperature (T_g)

As a result of the T_g dependence of the activation energy for transport (E_D), increased chain mobility will enhance the crystallization rate. In addition, upon decreasing the T_g , also a lower mold surface temperature will suffice during injecting molding. Consequently, the T_g is an important parameter for influencing the crystallization behavior of the PET-POTM block copolymer.

In comparison with the homopolymer, the polyether containing PET shows, as mentioned before, a lower hard segment T_g .⁸ This T_g depression of the hard phase can be explained¹⁸ by: the hard segment molecular weight dependence of T_g ; a consequence of surface-free volume; dynamic coupling of mobile soft segment chains to the hard microdomains. A further T_g depression can be achieved by:

— A reduction of the polyether molecular weight,¹⁹ resulting in a decreased PET segment length and hence in an increased mobility.

— Cocondensation of a flexible second dicarboxylic acid or "short chain" diol*, which sometimes provides a certain internal plasticizing effect.²⁰ However, depressing the T_g in this way does not guarantee an increased crystallization rate,²¹ because T_m is lowered as well (see the growth rate equation). Furthermore, the overall crystallinity will be lowered, with negative consequence for properties such as hardness, modulus, etc.²² Moreover, POTM as such can be regarded as an internal plasticizer.^{13,14,23}

— Use of an external plasticizer. At least in the case of the PET homopolymer it has met with a lot of success (especially) in combination with effective nucleating agents.

* Being no polyether, e.g., 1,4-bis(hydroxymethyl)-cyclohexane.

Influence and Improvement of the Nucleation

Prior to crystallizing, nucleation has to take place. It is known that the amount of (homogeneous) nuclei in the melt of the related PBT-POTM block copolymer can be raised in two ways: by increasing the hard segment content of the elastomer;^{22,24} by decreasing the temperature,^{7,22} which is in agreement with the growth rate equation since the nucleation term $[-CT_m^0/T(T_m^0 - T)]$ then becomes less negative ($T_m^0 - T$, being the undercooling, becomes larger).

Similar effects can be expected for a PET-POTM copolymer. From the growth rate equation it can also be derived that at *high* temperatures the contribution of the transport term ($-E_D/RT$) to the spherulite growth rate is very important (less negative). Hence, we have to accomplish a shift of the nucleation to higher temperatures. In this respect Bier²⁵⁻²⁷ was able to improve the crystallization of the PET homopolymer by cocondensation of minor amounts (approximately 5 mol %) of selected branched codiol units such as those of 3-methyl-pentanediol-2,4. On the analogy of these findings the same might be applicable to the PET-POTM block copolymer.

In general, heterogeneous nucleation is by far more effective than homogeneous nucleation. Improvement of the crystallization of the PET-POTM block copolymer^{6,8} by means of the addition of nucleating agents, such as calcium fluoride,²⁸ is well known. Reactive agents such as the sodium or potassium salts of stearic acid, montanic acid ($C_{27}H_{55}COOH$), dimer acid,[†] trimer acid,[†] alkyl-substituted succinic acids, polyhydric phenols, etc., are also mentioned for this elastomer in the patent literature.²⁹⁻³⁶ Legras et al.^{37a} and Garcia^{37b} have shown that it is likely that nucleation by means of such salts proceeds via a chemical reaction. The polymer undergoes chain scission to form polymeric species with ionic end groups which aggregate to form the true nucleating species. The concomitant increase of the melt strength upon addition of such salts to block copoly(ether ester)s, reported in the patent literature,³⁶ gives further substantiation of this view. This way of nucleation has been given the term "chemical nucleation."

Because of its convenience of application, especially the "chemical nucleation" in conjunction with plasticizers, has drawn our attention to encourage the crystallization of the PET-POTM block copolymers. Therefore, this method has been studied most extensively and will be a main item in this article.

EXPERIMENTAL

Materials

The block copolymers have been synthesized by ester interchange in the molten state from dimethyl terephthalate (DMT), alkylene diol (ethylene glycol or 1,4-butane diol), and polyoxytetramethylene diol with a molecular weight of about 1000, followed by melt polycondensation under vacuum.

[†] Dimer acid and trimer acid are the dimerization, respectively, trimerization, products of unsaturated C_{18} fatty acids such as linoleic and linolenic acid.

Upon use of 1,4-butane diol, both the ester interchange and melt polycondensation have been catalyzed by a Ti catalyst. For the ester interchange with ethylene glycol and subsequent polycondensation; however, a Zn and an Sb catalyst, respectively, are preferred. By using different amounts of polyether diol and DMT during the preparation, the ratio between hard and soft segments may be varied considerably. The compositions used and relative viscosities (η_{rel}) of the polymers (1% m/m in *m*-cresol at 25°C) are given in the tables.

Prior to injection molding, nucleating agents have been added to the polymers by means of precipitation from solution (mostly aqueous) on the granules. Absorption of plasticizers by the granules has been accomplished at 90°C.

Methods

For a proper investigation of the crystallization behavior of the PET-POTM block copolymer, three important conditions must be satisfied:

a. The experimental conditions (mold-surface temperature, residence time, etc.) have to be chosen with care in order to obtain test specimens with a relatively low crystallinity. In this way (small) improvements induced by modifications of the resin can be studied best. Furthermore, the molding must be stored at low temperature to prevent changes in crystallinity (post-crystallization takes place at room temperature) prior to analysis.

b. Sampling for subsequent crystallinity analysis must in each case be performed in exactly the same place of the test specimens.

c. It is most important that a suitable analysis method should be available to measure accurately the crystallinity parameters of the test specimens. A technique giving an excellent insight into the crystallinity state of the specimens is differential scanning calorimetry (DSC). A DSC curve may provide among other things the following information: T_{∞} is the temperature of cold crystallization during the heating run; ΔH_{cc} , the heat of cold crystallization during the heating run; T_{rc} , the temperature of recrystallization from the melt during the cooling run; ΔH_{rc} , the heat of recrystallization from the melt during the cooling run. The $\Delta H_{cc}/\Delta H_{rc}$ ratio is a measure of the crystallinity of the specimen. A ratio other than zero is indicative of incomplete crystallization in the molded part. An example of one of the thermograms obtained is shown in Figure 1. DSC conditions used are: equipment, Mettler TA-2000B system; sample size, 15 ± 1 mg; sample holder, Al crucibles; temperature program, heating the sample at a rate of 20°C/min from -80 to 30°C above the melting point T_m , maintaining it there for 3 min and finally cooling it at the same rate to room temperature; gas flow, N₂, 45 mL/min. 1/16 in. UL-94 test bars, needed for the DSC analysis, have been obtained by means of injection molding with an Arburg All-rounder 221/55-250 with an injection retardation of 1.3 and an open nozzle with decompression. The pertinent data are: Barrel temperature (°C), 240–275 (depending on resin composition); nozzle temperature (°C), 240–270 (depending on resin composition); mold temperature (°C), 50; injection + back pressure time (s), 12.0; cooling time (s), 18.0; release time (s), min 2.0; Screw revolution (rpm), 200; Back pressure (bar), 50.

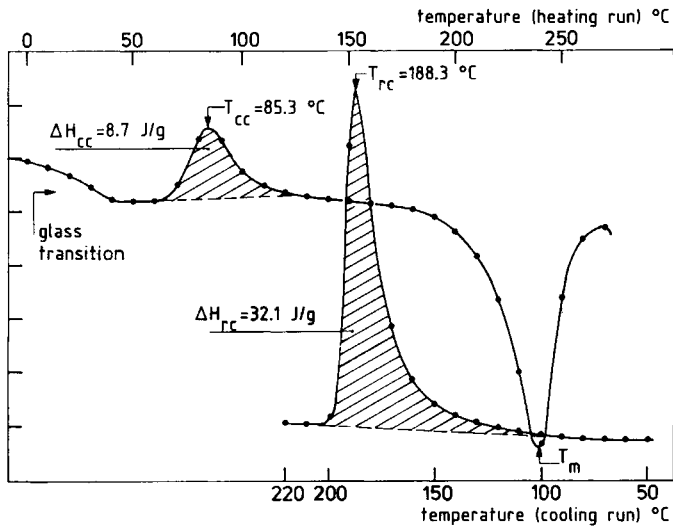


Fig. 1. DSC curves of expt no. 2.13.

Directly after mold release the test bar was quenched by means of liquid nitrogen and subsequently stored in a refrigerator at -30°C . Due to, *inter alia*, the skin-core morphology of the test bars,³⁸ the sampling position in the bar is important. Sampling has been achieved by cutting a small specimen from the middle of the test bar at a position 12 mm away from the gate.

The tensile properties were measured on an Instron universal testing machine (Model 1121) at a constant crosshead speed of 50 cm/min. Measurements were carried out on five samples collected under identical processing conditions, and the average value was calculated. The dynamic mechanical properties were determined, using a Rheometrics mechanical spectrometer, at 1 Hz and a maximum strain of 0.2% at temperature intervals of 5°C .

RESULTS AND DISCUSSION

Improvement of the Nucleation

Attempts have been made to improve the homogeneous nucleation of the PET-POTM copolymer by cocondensation of minor amounts of butanediol-1,4 or 2-methylpentanediol-2,4 (6.5 and 1.0 mol %, respectively, on DMT). On the analogy of the results obtained with the homopolymer by Bier,²⁵⁻²⁷ a codiol concentration of 5 mol % on DMT is presumed to be optimum. Higher concentrations cause a lower overall crystallization rate and crystallinity.³⁹ Owing to the low reactivity of the 2-methylpentanediol-2,4, only 1 mol % instead of 5 mol % of this diol appears to have been coesterified, however. This implies that for the higher content of 5 mol % a large excess of this hindered diol has to be used during the transesterification with DMT. The DSC results obtained with these modified elastomers are summarized in Table I. According to the DSC data the 2-methylpentanediol-2,4 modified

TABLE I
 DSC Data of Modified PET-POTM Block Copolymers

Expt. no.	Hard/Soft ^a ratio elastomer	Coesterified diol (mol %)	Sodium benzoate (%)	η rel molding	T_{rc} (°C)	T_{cc} (°C)	$\frac{\Delta H_{cc,b}}{\Delta H_{rc}}$
1.1	74/26	—	—	2.18	159.6	84.9	0.62
1.2	74/26	—	0.15	1.94	187.1	79.7	0.13
1.3	70/30	Butane ^c (6.5)	—	2.07	152.2	93.0	0.68
1.4	70/30	Butane ^c (6.5)	0.15	2.14	172.6	87.7	0.56
1.5	70/30	Pentane ^d (1.0)	—	2.08	187.2	87.0	0.34
1.6	70/30	Pentane ^d (1.0)	0.15	2.01	189.4	85.8	0.15

^a According to analysis data.

^b Measure of amorphous hard block content.

^c Butanediol-1,4.

^d 2-Methylpentanediol-2,4.

elastomer shows a better homogeneous nucleation (expt no. 1.5) than the unmodified elastomer (expt no. 1.1) in that the recrystallization temperature of 187.2°C is high with respect to that of the blank experiment ($T_{rc} = 159.6^\circ\text{C}$). Consequently, the corresponding $\Delta H_{cc}/\Delta H_{rc}$ value is low with respect to the value of the blank.

Heterogeneous nucleation by means of sodium benzoate lowers the $\Delta H_{cc}/\Delta H_{rc}$ values of the modified and unmodified polymers to the same level, indicating that modification of the elastomer by means of 2-methylpentanediol-2,4 influences only the nucleation (term), but not the transport (term). According to the results of expt nos. 1.3 and 1.4, modification by means of butanediol-1,4 influences the crystallization behavior very negatively. Even upon use of an effective heterogeneous nucleant practically no improvement has been observed, i.e., the test bars remain transparent (amorphous) without an elastomeric character.

The DSC data compiled in Table II substantiate the earlier finding that sodium benzoate is an effective nucleating agent (high T_{rc} value). As a contrast, the aluminum tristearate shows no activity. The (slightly) higher T_{rc} with respect to the blank expt no. 2.1 can be attributed to the decreased η_{rel} . Disodium tartrate is slightly less effective than sodium benzoate despite its enhanced sodium content (doubled). In addition, a serious brown discoloration has been observed. Sodium salicylate is, according to our data, nearly equivalent to sodium benzoate. The test bars obtained, however, prove to be slightly brown.

The results obtained with sodium montanate ($C_{26}-C_{32}$ carboxylate, supplied by Hoechst) prove that this salt is one of the most effective nucleating agents. In contrast with the benzoate, the sodium montanate shows a relatively low melting point of approx. 230°C. This implies a liquid state under processing conditions, which possibly means an increased reactivity compared with that of a sodium salt which is in the solid state.

From a comparison of the DSC-data of expt nos. 2.11–2.14, it can be concluded that the diepoxide Epikote 1007 is effective as conucleant, since it lowers the $\Delta H_{cc}/\Delta H_{rc}$ value, whereas the T_{cc} value is not (it therefore cannot be considered a normal plasticizer). Whether this is a question of synergism (Epikote 1007 is a weak nucleating agent⁴⁰) cannot be derived from these data.

Influencing the Crystallization by Means of Plasticizers

Table II clearly shows the merits of the use of neopentylglycol dibenzoate (NPGD). An increased spherulite growth rate is likely.⁴¹ Only in the case where no (effective) nucleant is present will the accelerator not be able to influence the $\Delta H_{cc}/\Delta H_{rc}$ ratio despite the lowered T_{cc} value (indicating[†] a lowered T_g ; compare expt nos. 2.5 and 2.4). A similar situation is encountered in the case of deactivation of the nucleating agent by the plasticizer, experiment no. 3.1 shows this situation (see Table III). As compared with expt. no. 2.11, the $\Delta H_{cc}/\Delta H_{rc}$ ratio has enhanced, while the T_{rc} is somewhat

[†] The glass transition can be observed just before the cold crystallization exotherm (see Fig. 1). An increase of the T_g also results in an enhanced T_{cc} .

TABLE II
DSC Characteristics of PET-POTM Elastomers Containing Nucleants and a Crystallization Accelerator

Expt. No.	Hard/soft ratio elastomer	Nucleant	Accelerator ^a	η_{rel} molding	T_m (°C)	T_{cc} (°C)	ΔT_{cc}^b (°C)	$\frac{\Delta H_{cc}}{\Delta H_m}$
2.1	76/24 ^d	—	—	2.16	168.1	96.9	—	0.76
2.2	76/24 ^d	0.15% Na benzoate	—	2.11	185.2	85.6	—	0.45
2.3	76/24 ^d	0.15% Na benzoate	3% NPGD	1.98	186.7	80.7	4.9	0.29
2.4	76/24 ^d	0.91% Al stearate ^e	—	1.72	176.8	88.2	—	0.68
2.5	76/24 ^d	0.91% Al stearate ^e	3% NPGD	1.74	176.4	84.4	3.8	0.68
2.6	76/24 ^d	0.24% diNa tartratedihydrate ^e	—	2.10	186.2	88.9	—	0.55
2.7	76/24 ^d	0.24% diNa tartratedihydrate ^e	3% NPGD	2.01	186.2	80.2	8.7	0.23
2.8	76/24 ^d	0.17% Na salicylate ^e	—	2.10	184.2	86.2	—	0.48
2.9	76/24 ^d	0.17% Na salicylate ^e	3% NPGD	2.01	185.7	81.8	4.4	0.29
2.10	76/24 ^d	0.47% Na montanate ^f	—	2.04	187.0	82.1	—	0.29
2.11	76/26 ^g	0.15% Na benzoate	—	2.04	187.2	85.4	—	0.41
2.12	76/26 ^g	0.15% Na benzoate	3% NPGD	1.94	188.3	81.7	3.7	0.21
2.13	76/26 ^g	0.15% Na benzoate	—	2.01	188.3	85.3	—	0.27
2.14	76/26 ^g	1.0% Epikote 1007 ^h	—	—	—	—	—	—
		0.15% Na benzoate	3% NPGD	1.99	185.3	79.7	5.6	0.24
		1.0% Epikote 1007 ⁱ	—	—	—	—	—	—

^a Benzoflex S312 = neopentylglycolbenzoate = NPGD.

^b T_{cc} difference with respect to same exp. without accelerator.

^c Measure of amorphous hard block content.

^d Data are on the basis of analysis; on intake 69/31.

^e Equimolar with 0.15% Na benzoate.

^f Estimated equimolar.

^g Data are on the basis of analysis; on intake 69/31.

^h Powder.

ⁱ Granules.

TABLE III
DSC Characteristics of PET-POTM Elastomer Containing 0.15% Sodium Benzoate and a Crystallization Accelerator

Expt. No.	Hard/soft ratio elastomer	Accelerator	$\eta_{rel.}$ molding	T_{rc} (°C)	T_{cc} (°C)	ΔT_{cc}^a (°C)	$\frac{\Delta H_{cs,b}}{\Delta H_{rc}}$
2.11	74/26 ^c	—	2.04	187.2	85.4	—	0.41
2.12	74/26 ^c	3% NPGD ^d	1.94	188.3	81.7	3.7	0.21
3.1	74/26 ^c	3% Tris(β,β' -dichloropropyl)phosphate ^e	1.99	184.7	91.6	-6.2	0.67
3.2	74/26 ^c	3% Diphenylcresylphosphate ^f	2.10	179.7	82.1	3.3	0.55
3.3	74/26 ^c	3% Tricresylphosphate	1.99	183.9	80.9	4.5	0.40
3.4	74/26 ^c	3% Carbothoxymethyl(diethylphosphonate (PEE))	1.87	185.7	83.5	1.9	0.61
3.5	74/26 ^c	3% Butylbenzylphthalates ^g	1.99	185.9	78.8	6.6	0.35
3.6	74/26 ^c	3% Benzylcetyl adipate ^h	1.98	188.8	79.3	6.1	0.25
3.7	74/26 ^c	3% Diisooctylphthalate	1.99	187.5	82.6	2.8	0.32
3.8	74/26 ^c	3 Diethyleneglycoldibenzoate ⁱ	1.88	190.3	77.7	7.7	0.13
3.9	74/26 ^c	3% Triethyleneglycoldi-caprate/caprylate ^j	1.74	193.6	74.6	10.6	0.08
3.10	74/26 ^c	3% Diphenylether	1.99	186.6	78.9	6.5	0.25
3.11	74/26 ^c	3% Poly- <i>m</i> -phenyleneoxide (<i>n</i> = approx. 9)	1.96	187.5	84.4	1.0	0.27
3.12	74/26 ^c	3% Diphenylamine	1.85	189.0	77.2	8.0	0.17
3.13	74/26 ^c	3% Triphenylamine	1.91	186.9	81.5	3.7	0.37
3.14	74/26 ^c	3% Benzophenone (diphenylketone)	1.97	186.2	77.9	7.5	0.17

3.15	74/26 ^c	3% Diphenylsulfone	1.97	185.4	82.4	3.0	0.33
3.16	74/26 ^c	3% Dimethylsulfone	1.93	186.8	84.0	1.2	0.37
3.17	74/26 ^c	3% <i>N</i> -ethyl- <i>o,p</i> -toluenesulfonamide ^k	1.96	187.9	79.6	5.8	0.26
3.18	74/26 ^c	3% Succinimide	1.81	190.1	82.1	3.1	0.23
3.19	88/12 ^l	—	1.71	194.8	101.8	—	0.52
3.20	88/12 ^l	3% NPGD ^d	1.69	195.5	96.4	5.4	0.42
3.21	70/30 ^m	—	2.09	173.2	88.6	—	0.81
3.22	70/30 ^m	3% NPGD ^d	2.00	175.6	77.3	11.3	0.64
3.23	70/30 ⁿ	—	1.81	194.2	83.3	—	0.11
3.24	70/30 ⁿ	3% NPGD ^d	1.72	195.5	77.3	6.0	0.07

^a T_{∞} difference compared with expt. without accelerator.

^b Measure of amorphous hard block content.

^c Data are on the basis of analysis; on intake 69/31.

^d Benzoflex S312 = neopentylglycoldibenzoate = NPGD.

^e Fyrol FR-2.

^f Disflamol DPK.

^g Santicizer 160.

^h Adimol BO.

ⁱ Benzoflex 245.

^j Bisoflex 102.

^k Santicizer 8.

^l Data are on the basis of analysis; on intake 80/20.

^m On the basis of intake, according to analysis data the hard block contains also 7.3 mol % butanediol (on DMT).

ⁿ Data on the basis of analysis, the hard block contains 1.0 mol % 2-methylpentanediol-2,4.

lower. Consequently, it can be concluded that the sodium benzoate has been deactivated. Though the tris (β,β' -dichloropropyl)phosphate cannot be regarded as a plasticizer in view of its negative ΔT_{cc} value, the other phosphorus compounds used (in expt nos. 3.2–3.4) apparently enhance the flexibility of the polymer chain, resulting in a decrease of the T_{cc} , nevertheless, the $\Delta H_{cc}/\Delta H_{rc}$ values are high owing to deactivation of the sodium benzoate. This is substantiated by the relatively low T_{cc} values.

Also the results obtained with a normal carboxylic acid ester such as butyl benzylphthalate indicate that other plasticizers (or impurities in it) may deactivate the nucleant used. The observed too high $\Delta H_{cc}/\Delta H_{rc}$ value in expt no. 3.5, in view of the lowered T_{cc} ($\Delta T_{cc} = 6.6^\circ\text{C}$, compared with a ΔT_{cc} value of only 3.7°C giving $\Delta H_{cc}/\Delta H_{rc} = 0.21$ in expt. no. 2.12), reflects this deactivation. Again, this is also substantiated by a decreased T_{rc} .

The use of certain esters as accelerators shows an additional disadvantage, viz., the possibility of transesterification causing degradation of the polymer. The very low η_{rel} in expt nos. 3.8 and 3.9 reflects this transesterification. As expected, low $\Delta H_{cc}/\Delta H_{rc}$ values and high T_{rc} were detected. Even esters which do not easily transesterify, such as those with a neo-structure (NPGD in expt no. 2.12) degrade the polymer. Consequently, it is preferred to choose inert accelerators, e.g., diphenylether or poly(*m*-phenyleneoxide) (expt nos. 3.10 and 3.11). As can be seen from the table, these ethers are effective accelerators. Although the volatility of the diphenylether can be regarded as a disadvantage, its nonvolatile oligomeric form, viz., poly(*m*-phenyleneoxide), suffers from another shortcoming, namely there is hardly a shift of the crystallization range to lower temperatures ($\Delta T_{cc} = 1.0^\circ\text{C}$). Nevertheless, the $\Delta H_{cc}/\Delta H_{rc}$ values observed in expt no. 3.11 is rather low. The poly(*m*-phenyleneoxide) probably belongs to the group of internal lubricants, since these lubricants are considered to be pseudo-plasticizers at processing temperatures, thus reducing the van der Waals forces between polymer chains.⁴² This reduction encourages sufficient chain mobility to crystallize at a relatively high rate. Unlike plasticizers, however, these effects must be negligible at ambient temperatures, and become significant only at melt temperature, perhaps because of increased compatibility. Since the plasticizing effect of this crystallization accelerator is negligible at ambient temperatures, the T_g and T_{cc} of the elastomer are hardly effected. In view of the similarity between the molecular structure of poly(*m*-phenyleneoxide) and Epikote 1007 (both compounds are oligomeric aromatic polyethers) and because of their similar influence on crystallization behavior, it might be presumed that Epikote 1007 is a pseudo-plasticizer (internal lubricant) rather than a synergistic nucleating agent (see the foregoing section). We have, however, indications that even cocondensed Epikote 1007 is effective, indicating that also other mechanisms can be operative.

Apart from its reactivity, diphenylamine shows some resemblance to diphenylether (compare expt. nos. 3.12 and 3.10). The same holds for benzophenone (expt no. 3.14). Compounds, however, containing a sulfone group instead of a functional group such as keto, amino, or ether group, do not prove to be very effective (expt nos. 3.15 and 3.16). On the other hand, the sulfonamide "Santicizer 8" is one of the better nonvolatile accelerators (expt no. 3.17). Succinimide, in turn, is not very effective.

The PET-POTM block copolymer used in expt nos. 3.19 and 3.20 contains a higher hard segment content. Due to the increased T_c 's, injection molding under the same conditions (mold temperature 50°C) led to moldings with a relatively decreased crystallinity. The introduction of 7.3 mol % butanediol-1,4 into the hard segments of the elastomer again results in a dramatically decreased overall crystallization rate (high $\Delta H_c/\Delta H_\infty$ value), as can be seen from the data of expt nos. 3.21 and 3.22. The heat of crystallization (not included in the table) indicates that also the crystallinity has decreased by approx. 20% owing to the introduction of the codiol. Upon introduction of 1 mol % 2-methylpentanediol-2,4 these negative effects were not observed (expt nos. 3.23 and 3.24).

Influence of Crystallization on Mechanical Properties

In order to investigate the influence of parameters such as mold surface temperature and amount of crystallization accelerator (NPGD) on the injection molding behavior and mechanical properties, experiments have been performed on Arburg Allrounder and Stübbe injection-molding machines. The results are summarized in Tables IV and V. According to these data the tension set is positively influenced by the use of more plasticizer and higher mold surface temperatures. This is a result of the enhanced crystallinity, giving a relatively more "physically crosslinked" system. Also properties such as modulus and yield stress are basically controlled by the degrees of crystallinity.⁷ This is confirmed in Table IV, since samples injection-molded at a mold surface temperature of 90°C show the highest yield stress. The flexural modulus increase due to the addition of a small amount of plasticizer (3% NPGD), observed in Table V, reflects also a crystallinity increase owing to an enhanced crystallization rate or a structural after-arrangement caused by the plasticizer, a phenomenon which has been referred to as "antiplasticization."⁴³ Apparently, upon the addition of even more plasticizer (5% NPGD) real plasticization becomes more important, leading to a drop in modulus. In accordance with the data of Table IV, also the tension set data in Table V show an improvement upon the use of plasticizer, whereas the tensile strength and the tear propagation energy decrease. The latter data are in agreement with those of Table IV, and give further substantiation of earlier findings, viz., failure properties, such as tensile strength, etc., depend on the details of morphology rather than on the degree of crystallinity.

In view of the observed hardness increase upon storage (see Table IV), it has to be concluded that the crystallinity has not been optimum yet. Of course, also annealing enhances the crystallinity (see also the next section). From the injection-molding experiments we infer that a mold surface temperature of at least 70°C is required to obtain optimum mechanical properties. In comparison with the fast crystallizing PBT-POTM elastomer, the cycle time for the PET-POTM copolymer will be 20–40% longer, depending on the molding dimensions, while injection-molding processing conditions are more critical than those of the analogous PBT-POTM copolymer. It should be stressed that injection molding, under the same conditions, of PET-POTM without nucleating agents results in amorphous moldings.

TABLE IV
Influence of Mold Surface Temperature and Plasticizer Content on Some Properties of a PET-POTM Elastomer^a

Properties	Method	Additives											
		0.15% Na benzoate 1% NPGD			0.15% Na benzoate 2% NPGD			0.15% Na benzoate 3% NPGD			0.15% Na benzoate carnauba wax		
Mold surface temperature	(°C)	90	70	50	90	70	50	90	70	50	90	70	50
Hardness													
After 24 h (Shore D)	DIN 54505	61	59	60	60	59	59	58	58	59	58	58	59
After 2 weeks (Shore D)	DIN 53505	62	63	63	62	62	62	61	62	62	61	62	62
After annealing for 30 min	DIN 53505		68			67			63				
at 140°C (Shore D)													
Tensile strength (MN/m ²)	ISO R 527	40.7	42.4	43.7	38.4	40.7	42.3	39.4	41.7	42.1	41.7	42.1	42.1
Elongation at break (%)	ISO R 527	515	567	570	449	565	553	569	556	585	569	556	585
Tension set, 100% strain (%)	ASTM D412	73	76	82	71	73	76	64	62	65	64	62	65
Tear resistance Graves (KN/m)	DIN 53151	183	172	170	177	174	169	176	169	165	176	169	165
Tearing energy Graves (J)		10.1	9.6	9.9	7.7	8.5	10.1	9.1	9.1	9.3	9.1	9.1	9.3
Tear resistance (propagation) (KN/m)	ASTM D1938	88	95	92	86	88	98	77	79	90	77	79	90
Tear propagation energy (with incision) (J)		9.3	9.9	10.5	8.9	9.3	10.2	8.1	8.4	9.5	8.1	8.4	9.5

^a Hard-to-soft segment ratio is 74/26; η_{rel} , granules: 2.16.

TABLE V
Influence of Plasticizer Content on Some Properties of a PET-POTM Elastomer^a

Properties ^b	Method	Additives									
		0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate	0.15% Na benzoate
η_{sp}		2.67	2.52	2.52	2.52	2.65	2.65	2.65	2.65	2.65	2.64
Melt flow index, (250°C, 2160 g) (g/10 min)	ISO R1133	12	28	31	17	20	20	20	20	20	20
Hardness after 3 weeks (Shore D)	DIN 53505	57	54	52	54	52	52	52	52	52	54
Tensile strength (MN/m ²)	ISO R527	41.9	37.0	40.3	39.4	40.2	40.2	40.2	40.2	40.2	35.0
Elongation at break (%)	ISO R527	584	587	550	572	603	603	603	603	603	725
Flexural modulus (MN/m ²)	ISO 178	155	167	146	169	146	146	146	146	146	200
Charpy impact strength ^c (notched) at -30°C (kJ/m ²)	ISO 179	5x n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
-40°C (kJ/m ²)		15.4	15.7	17.4	15.6	21.6	21.6	21.6	21.6	21.6	n.b.
Tensile set 25% strain (%)	ASTM D412	38	33	31	36	33	33	33	33	33	36
100% strain (%)		58	52	48	51	50	50	50	50	50	55
HDT-B (0.46 MN/m ²) (°C)	ISO R75	57	58	58	57	56	56	56	56	56	89
Tear resist. Graves (KN/m)	DIN 53515	178	165	164	171	166	166	166	166	166	162.64
Tearing energy Graves (J)		11.5	10.1	9.9	10.6	10.1	10.1	10.1	10.1	10.1	8.0
Tear resistance tear propagation (KN/m)	ASTM D1938	99	81	71	90	71	71	71	71	71	84
Tear propagation Energy (with incision) (J)		10.9	8.6	7.4	9.9	7.7	7.7	7.7	7.7	7.7	8.3

^a Hard-to-soft segment ratio is 68/32.
^b Samples injection-molded at a mold surface temp of 90°C.
^c Hard-to-soft segment ratio is 65/35.
^d n.b. means no break.

Dynamic Mechanical Behavior

DSC thermograms of PBT-POTM block copolymers usually reveal one amorphous phase glass transition and at least one crystalline phase melting endotherm. In the case of copoly(ether ester)s containing POTM segments with an $M_n \geq 2000$, a second melting endotherm has been observed,¹⁹ owing to melting of these (crystallized) segments at 10–30°C. A rise in the concentration of polyether soft segment leads to a decreased T_g (see also Fig. 2, change in G'' max positions), and an increased heat capacity change through the glass-transition zone in DSC thermograms of PBT-POTM elastomers.²⁰ The fact that T_g shows a progressive shift with respect to hard segment content suggests that solubilized hard segments are included within the amorphous phase.^{1,20,44} Small-angle X-ray scattering measurements indicate also a homogeneous amorphous phase, though some heterogeneity is present.² Apart from the composition of the copolymer, the temperature position of the glass transition is also governed by the crystallization conditions, e.g., annealing causes a shift to lower temperatures.^{1,22,44}

The PET-POTM block copolymer offers very interesting possibilities for further investigation of the relation between the T_g observed and the content of amorphous PET segments, since in this case the content of amorphous material can easily be changed without altering the hard/soft segment ratio. The elastic or storage modulus, G' , and the dissipation factor, $\tan \delta$, of the quenched, amorphous PET-POTM elastomer (hard/soft segment ratio is 74/26, no nucleating agent present) are plotted as a function of temperature in Figure 3. The temperature where the $\tan \delta$ curvature

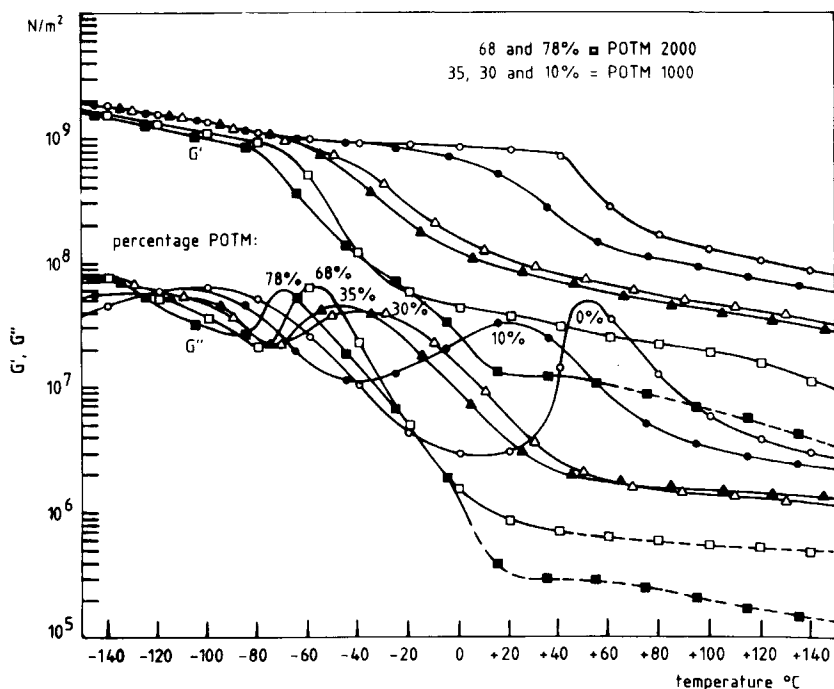


Fig. 2. G' and G'' of PBT-POTM elastomers containing different amounts of POTM.

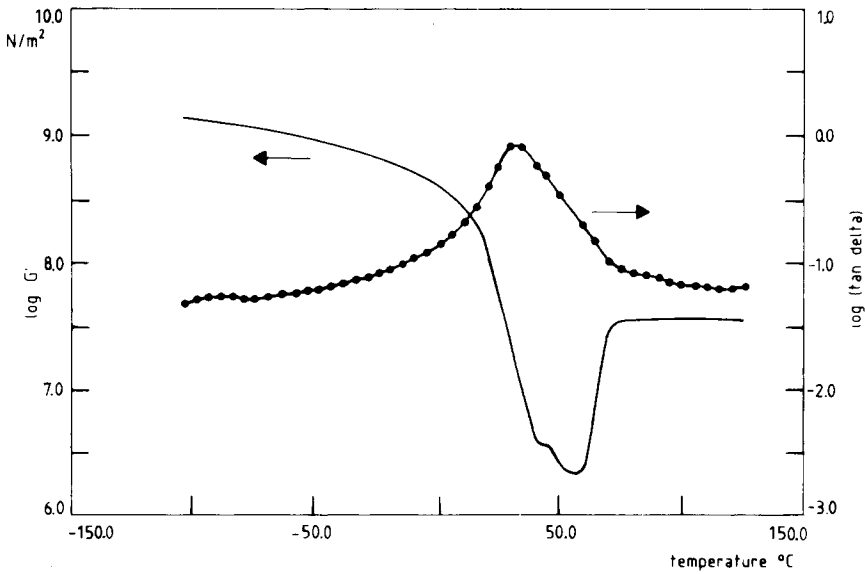


Fig. 3. Dynamic-mechanical spectrum (at 1 Hz) of amorphous PET-POTM elastomer, containing 26% (m/m) POTM.

shows its maximum (T_{β}^{\max}) may in a first approximation be called the glass-transition temperature. At about 20°C above the T_g , the hard segments crystallize in view of the steep increase in storage modulus. In spite of the corresponding change in amorphous phase composition, owing to crystallization of the hard segments, the T_{β}^{\max} practically did not change (compare Figs. 3 and 4). In addition, the $\tan \delta$ curvature is very broad and shows a shoulder at approx. -45°C, indicating the glass transition of POTM-rich

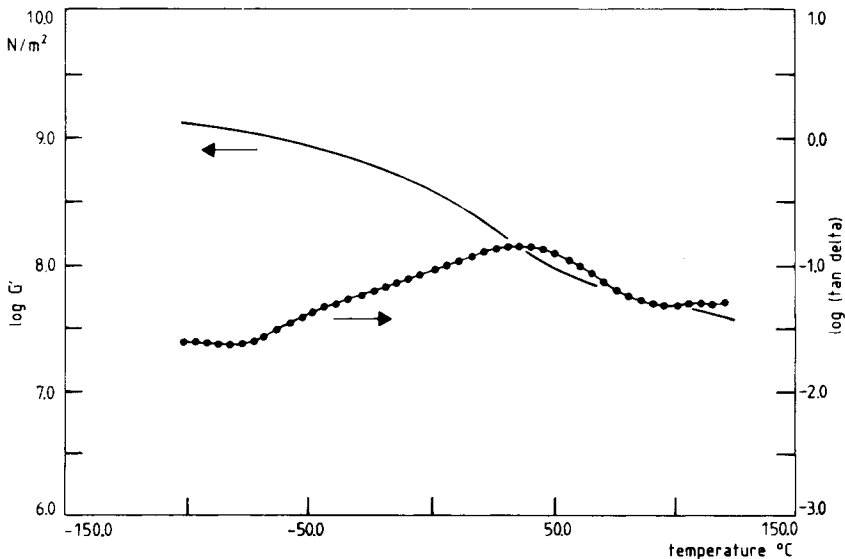


Fig. 4. Dynamic-mechanical spectrum (at 1 Hz) of crystallized PET-POTM elastomer containing 26% (m/m) POTM.

regions. The T_{β}^{\max} , therefore, indicates the glass transition of PET-rich regions (see also the glass transition in Fig. 1). Since there is no steep transition in the elastic modulus at -45°C (see G' curvature), the shoulder on the $\tan \delta$ curvature must be caused by a relatively small amount of POTM-rich material. Considering these aspects, we infer that the amorphous phase of the PET-POTM elastomer is heterogeneous. Since the amorphous PET regions are not mixed to large extent with POTM, partial crystallization will not drastically change the T_{β}^{\max} . Segmental incompatibility is higher in PET-POTM than in PBT-POTM, as indicated by the higher difference between the solubility parameters (calculated according to Ref. 45) of PET, $(20.9 \text{ J cm}^{-3})^{1/2}$, and POTM $(17.6 \text{ J cm}^{-3})^{1/2}$, than between the same parameters of PBT, $(19.6 \text{ J cm}^{-3})^{1/2}$, and POTM. Segmental incompatibility accounts for the larger extent of phase segregation between hard and soft segments observed in the amorphous part of PET-POTM with respect to PBT-POTM.

An increase in the elastic modulus G' upon crystallization of PET segments may be expected on the basis of the relationship²²

$$\log E = \nu_c \log(E_c/E_a) + \log E_a$$

where ν_c is the volume fraction crystalline material, while E_c and E_a are interpreted as the modulus of the crystalline and amorphous material. Crystallized PET-POTM samples (hard-to-soft segment ratio 68/32) containing 0.15% sodium benzoate and, whether or not, 5% NPGD (see also Table V) have also been investigated by means of dynamic mechanical analysis. Figures 5 and 6 show that the addition of plasticizer causes a T_g shift and a decrease of the modulus at room temperature. The $\tan \delta$ curvature of the nonplasticized sample even shows a more pronounced shoulder

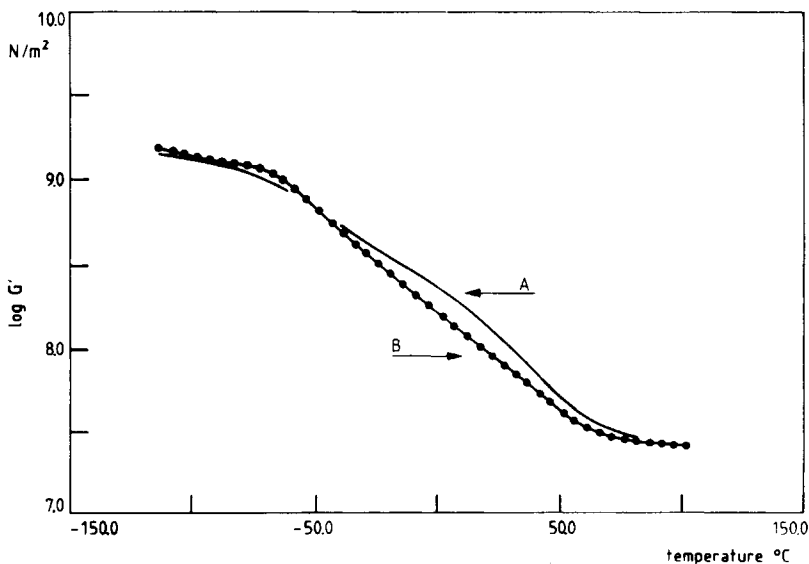


Fig. 5. Storage modulus of PET-POTM elastomers vs. temperature. Samples A and B contain 0 and 5% NPGD, respectively. The POTM content of both samples is 32% (m/m).

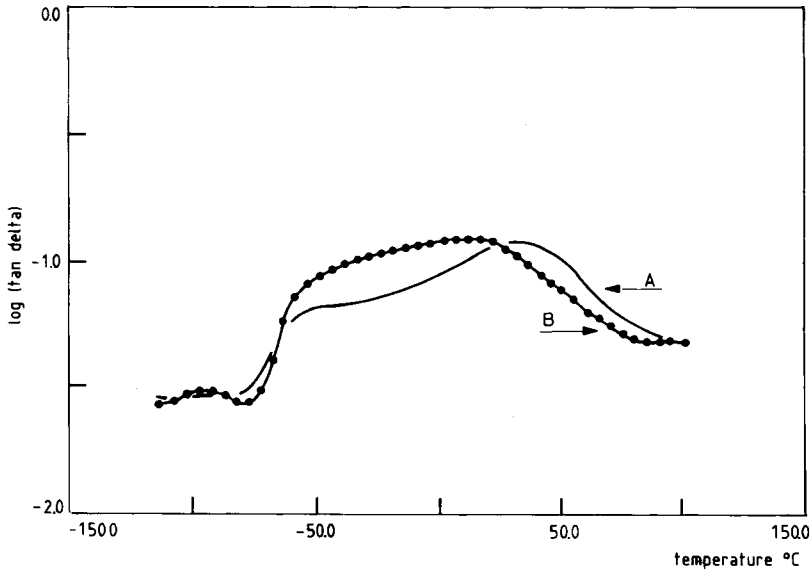


Fig. 6. Dissipation factor of PET-POTM elastomers versus temperature. Samples A and B contain 0 and 5% NPGD, respectively. The POTM content of both samples is 32% (m/m).

at -50°C , owing to the enhanced POTM content of this sample relative to the sample used in the case of Figures 3 and 4. In addition, the T_{β}^{max} of this softer grade has not changed to a lower temperature, giving further substantiation for a fairly good phase segregation between hard and soft segments. This also implies that a further increase in the POTM content probably will not improve the spherulite growth rate. From the measurement data (Fig. 7) of the PBT-POTM elastomer (hard to soft segment ration

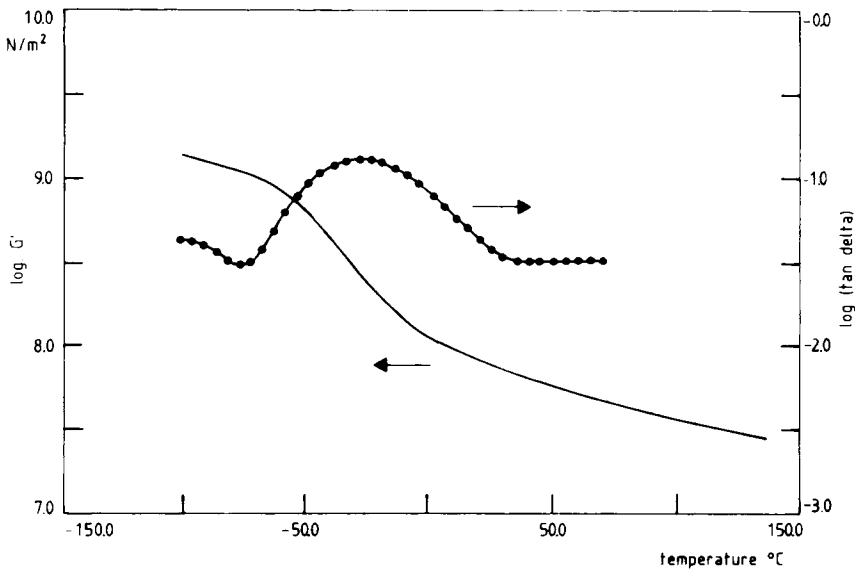


Fig. 7. Dynamic-mechanical spectrum (at 1 Hz) of PBT-POTM elastomer, containing 35% (m/m) POTM.

is 65/35; see also Table V) we infer that the T_{β}^{\max} of this elastomer is situated at a lower temperature than the T_{β}^{\max} measured for the corresponding PET-POTM elastomer, while the $\tan \delta$ curvature is sharper. With respect to the PET-POTM elastomer also the change in modulus upon temperature change in the range of -10 up to $+50^{\circ}\text{C}$ is less pronounced.

CONCLUSIONS

The crystallization behavior of the PET-POTM copolymer is positively influenced by selected nucleating agents whether or not in conjunction with plasticizers. Both sodium benzoate and sodium montanate exhibit a good performance as nucleant, while plasticizers such as NPGD and *N*-ethyl-*o*-*p*-toluenesulfonamide, in conjunction with the nucleant, accelerate the crystallization. Moreover, they shift the cold crystallization temperature of the segmented copoly(ether ester) to a lower level, which means that a lower mold temperature (80 – 90°C) will suffice for a proper hardening upon injection molding of this elastomer. Some classes of plasticizers, however, for example, phosph(on)ates, inhibit the (chemical) nucleation. Upon cocondensation of minor amounts of 2-methylpentanediol-2,4 the crystallization behavior of the elastomer proves to have improved. On the contrary, cocondensation of butanediol-1,4 give rise to products which suffer from a low rate of crystallization.

Nucleating agents and plasticizers added, as well as the molding conditions, strongly influence the (dynamic-) mechanical properties of the PET-POTM copolymer. Under optimum molding conditions the mechanical properties of this elastomer are similar to those of the PBT-POTM copolymer. Dynamic mechanical analysis of the PET-POTM copolymer indicates a larger extent of microphase separation with respect to that of the corresponding PBT-POTM copolymer. Two glass transitions are observed, indicating a heterogeneous amorphous phase.

The author wishes to thank Mr. T. Brink, Ir. A. J. Witteveen, Mr. A. C. M. Bockholts, Dr. E. A. A. van Hartingsveldt, Ir. P. J. M. Oerlemans and Mr. M. J. J. M. Hegeraat for their valuable contributions.

References

1. M. Dröscher et al., *Makromol. Chem., Suppl.*, **6**, 107 (1984), and references cited.
2. G. Perego et al., *J. Appl. Sci.*, **29**, 1157 (1984), and references cited.
3. W. K. Witsiepe, *Am. Chem. Soc., Polym. Prepr.*, **13**(1), 588 (1972).
4. W. K. Witsiepe, *Adv. Chem. Ser.*, **129**, 39 (1973).
5. J. R. Wolfe, *Am. Chem. Soc., Polym. Prepr.*, **19**(1), 5 (1978).
6. J. R. Wolfe, *Adv. Chem. Ser.*, **176**, 129 (1979).
7. L. Zhu and G. Wegner, *Makrom. Chem.*, **182**, 3625 (1981).
8. A. B. Ijzermans et al., *Br. Polym. J.*, **7**, 211 (1975).
9. F. J. Huntjens and J. A. A. Noordman, *Plastica*, **27**(10), 54 (1974).
10. D. Griffioen, *Plastica*, **31**(3), 66 (1978).
11. R. W. M. van Berkel et al., in *Developments in Block Copolymers 1*, I. Goodman, Ed., Applied Science, London, 1982, Chap. 7.
12. J. B. Jackson and G. W. Longman, *Polymer*, **10**, 873 (1969).
13. E.P. 0 029 285.
14. E.P. 0 021 648.
15. D. W. van Krevelen, in *Properties of Polymers*, Elsevier, Amsterdam, 1976, Chap. 19.

16. F. van Antwerpen, thesis, Technische Hogeschool Delft (1971).
17. L. R. Burke and J. M. Newcome, *ANTEC Soc. Plast. Eng. Tech. Pap.*, **28**, 336 (1982).
18. W. Gronski et al., *Makromol. Chem. Suppl.*, **6**, 141 (1984), and references cited.
19. C. M. Boussias et al., *J. Appl. Polym. Sci.*, **25**, 855 (1980).
20. A. Lilaonitkul and S. L. Cooper, *Rubber Chem. Technol.*, **50**, 1 (1977).
21. L. Szegö, *Adv. Polym. Sci.*, **31**, 89 (1979).
22. L. Zhu et al., *Macromol. Chem.*, **182**, 3639 (1981).
23. Y. Camberlin and J. P. Pascault, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 415 (1983).
24. U. Bandara and M. Dröscher, *Colloid Polym. Sci.*, **261**, 26 (1983).
25. P. Bier et al., *Angew. Makromol. Chem.*, **65**, 1 (1977).
26. Offenlegungsschrift 2 507 776.
27. Offenlegungsschrift 2 706 123.
28. DE 2 352 584.
29. (a) E.P. 0 51 220; (b) J. 52004-550; (c) J. 52039-747.
30. J. 57028-151.
31. J. 57036-124.
32. J. 57036-125.
33. J. 57047-347.
34. J. 57031-949.
35. J. 57059-948.
36. US. 4363-892.
37. (a) R. Legras et al., *Polymer*, **25**, 835 (1984); (b) D. Garcia, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 2063 (1984).
38. S. Y. Hobbs and C. F. Pratt, *J. Appl. Polym. Sci.*, **19**, 1701 (1975).
39. E. Ponnusamy et al., *Polymer*, **23**, 1391 (1982).
40. V.G.F. 1291.
41. V. V. Niznik and V. P. Salomko, *Acta Polym.*, **34**(8), 470 (1983).
42. *Encyclopedia of PVC*, L. I. Nass, Ed., Marcel Dekker, New York, 1976, p. 648.
43. B. P. Shtarkman and L. N. Razinskaya, *Acta Polym.*, **34**(8), 514 (1983).
44. G. Wegner et al., *Angew. Makromol. Chem.*, **74**, 295 (1978).
45. D. W. van Krevelen, in *Properties of Polymers*, Elsevier, Amsterdam, 1976, Chap. 7.

Received May 23, 1985

Accepted September 26, 1985