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Effect of aging on the mechanical properties of cold-crystallized poly(trimethylene terephthalate)

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Abstract

The changes in the mechanical and thermal properties of cold-crystallized poly(trimethylene terephthalate) during aging at 60 and 80 °C were investigated. A significant increase in the tensile modulus and stress at yield and a decrease in strain at yield were observed for both aging temperatures. Differential scanning calorimetry (DSC) scans of the aged sample showed an endothermic annealing peak 10–20 °C above the previous aging temperature, the maximum temperature and enthalpic content of these peaks increased with aging time. Dynamic mechanical measurements indicated a relaxation process starting at about 20 °C above the aging temperature and correlate with the annealing peak detected by DSC. Density measurements and wide-angle X-ray scattering investigation revealed that neither the crystallinity increased significantly nor did the crystal structure changed. These results were explained by the existence of a third phase besides the crystalline and the 'classical amorphous' which involves oriented and constrained 'non-crystalline' polymer chain sequences close to the crystalline lamellae.

Keywords: Aging; Mechanical properties; Poly(trimethylene terephthalate)

1. Introduction

The cooling of an amorphous polymer through the glass transition (T_g) results in a non-equilibrium glassy state that then proceeds to spontaneously evolve towards a temporally distant equilibrium [1,2]. Associated with the evolution of the state variables of, e.g. volume or enthalpy, are observable changes of macroscopic properties such as viscoelastic response, yield strength, impact resistance, etc. [3], which has come to be referred as *physical aging*. One anticipates similar behavior for the glassy response of semi-crystalline polymers. However, it has been observed that for semi-crystalline polymers physical aging persists even above the glass transition temperature [3–8]. A partial explanation for this behavior was offered by Struik [3–8]. His argument is based on the observation that in constant frequency experiments, in which the temperature is ramped from below to above the T_g, the loss factor (tan δ) of semi-crystalline polymers is broadened and appears to extend well above the T_g range of the equivalent amorphous polymer. Struik interpreted such behavior in terms of part of the amorphous phase being constrained by the presence of the crystalline regions, hence having a decreased mobility and correspondingly increased T_g. This model is also consistent with concepts of a *rigid* amorphous phase in semi-crystalline polymers. Consequently, physical aging could occur above the nominal T_g of the unconstrained amorphous fraction. Another complicating feature of aging of semi-crystalline polymers is the fact that recrystallization phenomena are possible above T_g [9], as this process is highly dependent on the molecular mobility of the amorphous phase.

Poly(trimethylene terephthalate) (PTT) has been recently introduced as a commercial polymer [10], joining the other aromatic polyesters, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). PTT is a rapidly crystallizing linear polyester with a crystalline melting temperature of 225 °C and a glass transition temperature (T_g) of ~40 °C [11]. The semi-crystalline solid polymer is an opaque rigid thermoplastic useful for many structural applications, e.g. in carpet, textile, film and packing and other engineering thermoplastic markets, where rigidity, strength and toughness are required. However, PTT,

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below or near its T_g, like other semi-crystalline polymers, undergoes a phenomenon of physical aging, involving changes in its polymer properties, that influences its performance and lifetime for fiber and engineering thermoplastic applications.

Since its commercial introduction in 1998 there is still a scarcity of useful information about the aging or crystallization of PTT [11,12], although some articles have been reported in very recent years [13–17]. Here we present some results on the aging of cold-crystallized PTT with respect to its mechanical and thermal properties and discuss the results with regard to proposed micro-structural changes.

2. Experimental

Powder PTT ($\bar{M}_n = 17300$ and $\bar{M}_w = 35200$, Shell Chemical Company) was compression-molded into ~1.0 mm thick sheet using a hot press at 250 °C. The material was kept in the melt for 10 min to erase any memory effects due to previous thermal history and was subsequently quenched in ice water. The sheet was cut into specimens of desired dimension. These specimens were isothermally cold-crystallized at 60 or 80 °C and stored at the respective temperature for various periods of aging time.

Density was determined using a density gradient column filled with the *n*-heptane/carbon tetrachloride mixture. Prior to placement into the column, samples were wetted with the liquid of composition corresponding to the upper part of the column. Accuracy of measurements was ±0.0005 g/cm^3.

Dynamic mechanical measurements were performed with a Seiko DMS 210 apparatus working in tensile mode at constant stress. The complex modulus, $E^* = E' + iE''$, of each sample was determined at 1 Hz over a temperature range 30–90 °C at a heating rate of 2 °C/min. Tensile testing were carried out using an Instron Dynamometer model 4301. Stress–strain curves were recorded at a strain rate of 10 mm/min.

To examine the thermal behavior of the aged PET samples a differential scanning calorimeter (DSC) from Polymer Laboratories was used. The instrument was calibrated with high purity melting standard (Indium and Zinc). All measurements were made under nitrogen conditions. To make certain that the thermal lag between the polymer sample and the DSC sensors is kept to a minimum, each sample holder was loaded with a single disk, weight around 4.0 ± 0.5 mg, which was cut from the as-prepared sheet. Wide-angle X-ray diffraction data were recorded with a Rigaku 40 KV rotating-anode X-ray generator (Cu K_α radiation) equipped with a diffractometer in the 2θ range 10–40°, using a scan speed of 2.0°/min.

3. Results

3.1. Mechanical results

Mechanical testing of PTT revealed the pronounced influence of aging on the mechanical properties. Fig. 1 shows the results of tensile modulus plotted against the logarithm of aging time for PTT samples aged at 60 and 80 °C, respectively. For both series the modulus increases with aging time. Compared to the value reached after one hour (this value is chosen as a reference here, as the testing time can then be considered short compared to the aging time), the modulus has increased by 100% at 60 °C after 1000 h. For the sample aged at 80 °C, the values of the modulus at shorter times are slightly higher but follow the same tendency. The change in mechanical behavior also manifests itself in a pronounced rise of stresses at yield, σ_y, accompanied by a decrease of strain at yield, ϵ_y. The characteristic values obtained are cited in Table 1. Representative stress–strain curves of aged PTT specimens are shown in Fig. 2. The curves are shifted on the horizontal axis, to be better visualized. Again compared to the values reached after one hour, σ_y has increased by 50% and ϵ_y has dropped by 25% at 60 °C after 1000 h.

Dynamic mechanical relaxation results at 30–90 °C are shown in Fig. 3a and b, respectively, for three PET samples of different age. For comparison we present also the results for the amorphous sample, i.e. PET sample measured directly after quenching. The amorphous exhibits a strong relaxation peak near 45 ° C corresponding to the glass transition of PTT [17] and a relatively small peak at ~62 ° C, which is also seen in the log E' versus temperature plot and is ascribed to the onset of cold crystallization during the non-isothermal scan. In the temperature range from 30 to 65 °C the storage modulus of the aged samples decrease less than that of the amorphous one as is known for semi-crystalline polymers. This decrease is more pronounced the

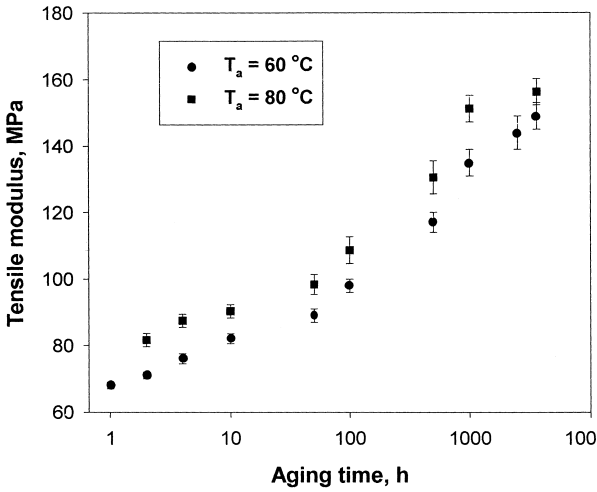

Fig. 1. Dependence of tensile modulus on the logarithm of aging time at 60 and 80 °C, respectively.

Table 1
Mechanical parameters derived from the stress–strain curves for aged PTT samples

Aging time (h)	$T_a = 60$ °C			$T_a = 80$ °C		
	E (MPa)	σ_y (MPa)	ϵ_y (%)	E (MPa)	σ_y (MPa)	ϵ_y (%)
1	68.2	8.3	11.3	–	–	–
2	71.4	8.6	11.4	81.6	11.2	14.8
4	76.5	9.1	11.1	87.4	11.8	14.4
10	82.1	9.7	10.7	90.3	12.6	13.9
50	89.3	10.4	10.0	98.3	13.5	13.0
100	98.6	11.1	9.2	108.7	14.4	11.9
500	117.3	11.9	8.4	130.5	15.4	10.9
1000	135.4	12.8	7.6	151.2	16.6	9.8
2500	144.7	14.3	6.6	–	–	–
3600	149.2	14.9	7.1	156.3	17.3	8.8

longer the material has been aged and consequently, the maximum of tan δ declines with aging time. Moreover, the results reveal a slight positive offset in glass transition for the aged specimens as compared to the wholly amorphous sample; the offset in T_g, namely $\Delta T_g = T_g^{\mathrm{ann}} - T_g^{\mathrm{am}}$, is nearly 8 °C for the sample aged for 100 h, and then remains almost constant with increasing aging time. This offset in T_g reflects the constraints imposed by the crystallites on the large-scale amorphous-chain motions inherent to the glass transition.

At a temperature between 65 and 90 °C, a second drop in the modulus curves of the aged material occurs; this accompanied by a second apparent relaxation process in tan δ plot. This second relaxation starts at about 20 °C above the aging temperature ($T_a = 60$°C) and is shifted to higher temperatures with longer aging time. This second relaxation might be correlated with the endothermic annealing peak seen in the DSC scans at the same temperature region; this will be discussed later.

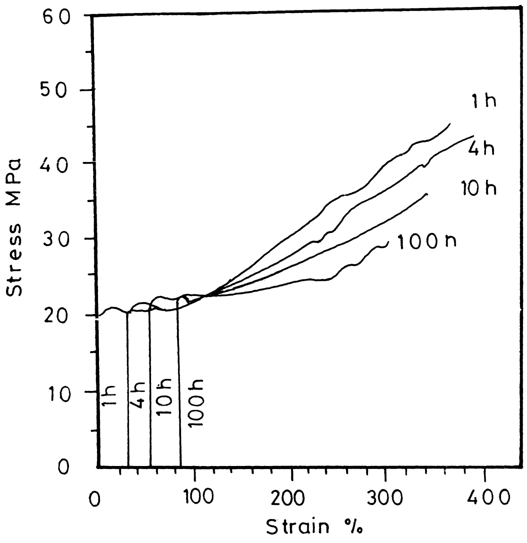

Fig. 2. Stress–strain curves of PTT samples aged at 60 °C for various time.

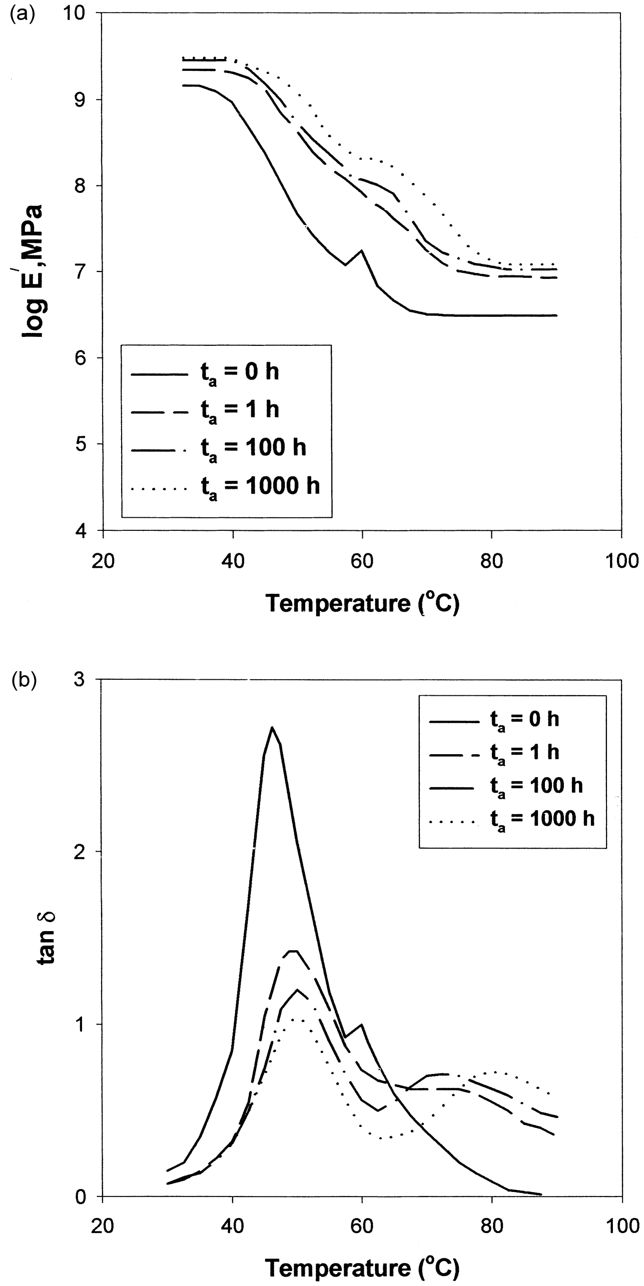

Fig. 3. Temperature dependence of (a) the storage modulus, and (b) loss tangent tan δ for PTT samples aged at 60 °C for various times.

3.2. DSC results

Fig. 4 shows the differential scanning calorimetry (DSC) scans of a rapidly quenched (150 °C/min) PTT and of PTT samples aged at different aging time ($t_a = 0, 1, 4, 100$ and 1000 h). When PTT is heated, the quenched sample shows a typical glass transition at 40 °C, a cold crystallization peak with a peak temperature of 60 °C and a melting peak at 228 °C. No exothermic crystallization peaks can be detected for the aged samples. Chuah [18] compared the isothermal crystallization kinetics of PET, PTT, and PBT and found PTT to crystallize at a rate in between those

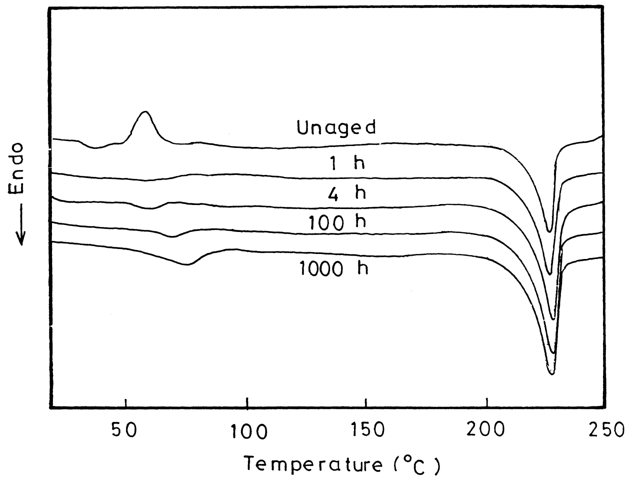

Fig. 4. DSC thermograms of PTT samples aged at 60 °C for various times.

of PET and PBT. PTT's Avrami rate constants were about order of magnitude faster than PET and an order of magnitude slower than PBT at the same degree of undercooling. Bulkin et al. [19], found when PTT was heated, the crystallinity increased at a much faster rate than PET in the rapid scanning Raman spectroscopy crystallization kinetics. At 71 °C, PTT crystallinity reached 80% of its equilibrium value in less than one minute while PET did not crystallize at all. With these findings, one can expect that the primary crystallization process be completed in a very short time much less than the aging time.

Regarding the scans of the aged samples, the glass transition has shifted to higher temperature and a second endothermic peak, i.e. annealing peak appears 10–20 °C above the aging temperature, whereas the position and the shape of the melting peak remain unchanged. The maximum temperature of the annealing peak as well as its enthalpy content increase with aging time. These observations have been found in some other semi-crystalline polymers [20–22], typically comprising a linear dependence of both, enthalpy and peak temperature, on the logarithm of annealing time.

3.3. Density and wide-angle X-ray results

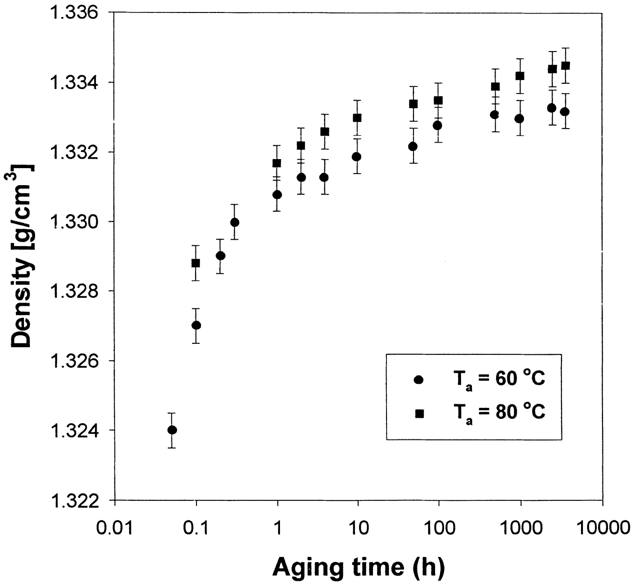

Fig. 5. Density of PTT samples aged at 60 and 80 °C versus logarithm of aging time.

The density is plotted versus the logarithm of aging time in Fig. 5. The diagram shows a sharp increase within the first minutes of aging due to crystallization setting in as soon as the samples are heated above their T_g. Further aging induces a slight linear increase in density with aging time. In contrast to the characteristic values describing the mechanical behavior (see Table 1), the increase in density is not very pronounced and in no account is sufficient to attribute the significant enhancement of mechanical properties during aging just to secondary crystallization. Fig. 6 shows wide-angle X-ray diffraction patterns of PTT sample measured directly after quenching and samples aged at 60 °C for different time. The unaged sample shows nearly no discernable diffraction peaks, indicating little crystallinity, whereas the aged samples exhibit sharper diffraction peaks. Comparing the scans of aged samples, no significant variations were observed as a function of time in the lattice parameters and the *d*-spacing values are almost constant for the observed crystallographic planes, which indicate no change in the crystal packing.

4. Discussion

The observed changes in the mechanical properties with aging time indicate that some kind of micro-structural reorganization take place within the material that does not preclude the possibility of secondary crystallization. However, apart from the first minutes, where structural arrangement is dominated by primary crystallization, the density does not increase considerably with aging time.

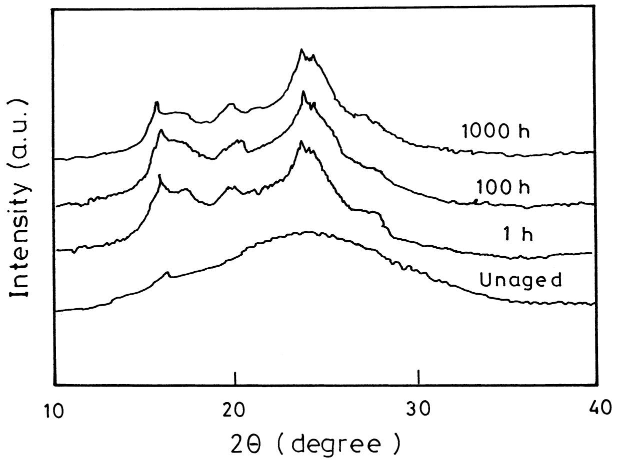

Fig. 6. WAXD pattern of PTT samples aged at 60 °C for various times.

Notably, the magnitude of this density effect is comparable to that observed in the physical aging of amorphous polymers [2] and cannot be attributed to secondary crystallization. Moreover, the possibility of more than two phases being present in the aged material implies that an increase in density does not necessary denote an increase in crystallinity. For two reasons the crystallinity calculated from these density values is not presented. Firstly, not the absolute values are of interest but a tendency should be shown, and secondly, calculating the crystallinity on the basis of density measurements implies the material consists of more than two phases, which may be an undue assumption in our case.

An another possible explanation for the development of the mechanical properties with time one might assume changes within the crystal, with the overall crystallinity remaining almost constant. Phenomena such as crystal perfecting or lamellar thickening, being a typical feature of many polymers at a temperature above the α_c-process. However, our DMA results over extended range of temperature (Figure not shown) does not show α_c-relaxation due to the crystalline phase, allowing no crystalline mobility at a temperature below the melting temperature. This excludes the possibility of crystal perfecting or lamellar thickening. Our wide-angle X-ray scattering (WAXS) experiments reveal no additional peaks in the diffraction pattern of the aged samples, indicating no change in the crystalline structure. So we conclude that the structure changes induced by aging does not affect the crystalline phase but take place within the amorphous regions or parts of the amorphous regions of the material.

Apparently, a reduction in the free volume as in the physical aging of amorphous polymer would explain the slight increase in density with time and would also affect the mechanical properties of the material; however, it would not account for such enormous increase of the modulus. On the other hand, the DMA results of the aged samples show a drop in the storage modulus starting at about 20 °C above the aging temperature; this accompanied by a second relaxation peak in the tan δ plot which shifts to a higher temperature with increasing aging time. The origin of this relaxation should be attributed to motions in the crystal-amorphous interphase. Thus, we assumes the presence of a third phase besides the crystalline and 'classical amorphous' which involves oriented and constrained 'non-crystalline' polymer chain sequences close to the crystalline lamellae. Moreover, the DSC scans of the aged samples show a small endothermic peak, which could be associated with the enthalpic recovery of a physically aged constrained amorphous fraction. Similar behavior have been observed in other semi-flexible polymers such as PET [23–26], poly(ether ether keton) (PEEK) [21,27,28] and poly(phenylene sulphide) [29]. Therefore we speculate that the dimensions of this ordered third phase in PTT increase with aging time and the small endotherm might represent their disordering. The growth of this phase with time might contribute to the slight increase in density and lead to the observed enhancement of the mechanical properties of the material.

It is worth mentioning that property changes occurring on physical aging are generally attributed to the relaxation process in the amorphous phase, leading to a reduction in enthalpy and free volume, which both be recovered at higher temperatures, implying that aging is a fully thermoreversible process [30]. To examine if PTT aged well above T_g shows similar behavior, annealing experiments were carried out. An annealing temperature of 100 °C was chosen, because it corresponds to the upper end of the annealing peak and from that temperature on DSC measurements revealed no change in the scans of the samples aged for different periods of time. So the aging-induced changes within the PTT can be seen as a thermoreversible process.

5. Conclusion

In this study the influence of aging above the glass transition on the mechanical properties of PTT has been investigated. Our results showed a significant enhancement of mechanical properties that cannot be attributed to secondary crystallization. We presume that aging result in the formation of a third phase besides the crystalline and the classical amorphous which involves oriented and constrained non-crystalline polymer chain sequences close to the crystalline lamellae. The growth of this phase with time might contribute to the slight increase in density and lead to enormous increase in the tensile modulus and the shift of the yield point towards higher stresses and lower strains as well as the appearance of an aging time dependent annealing peak in DSC scans. Efforts towards a deeper verification of this hypothesis as well as results concerning the kinetics of the aging process are in progress.

References

[1] Kovacs AJ. Fortsch Hochpolymer Forschung 1963;3:394.

[2] McKenna GB. In: Booth C, Price C, editors. Comprehensive polymer science. Polymer properties, vol. 2. Oxford, England: Pergamon; 1989. p. England.

[3] Struik LCE. Physical aging in amorphous polymers and other materials. Amsterdam: Elsevier; 1978.

[4] Struik LCE. Polymer 1987;28:1521.

[5] Struik LCE. Polymer 1987;28:1534.

[6] Struik LCE. Polymer 1989;30:799.

[7] Struik LCE. Polymer 1989;30:815.

[8] Spinu I, McKenna GB. Polym Engng Sci 1994;34:1808.

[9] De Koning GJM, Lemstra P. J Polym 1993;34:4089.

[10] Traub HL. Die Angew Makromol Chem 1995;179:4055.

[11] Pyda M, Boller A, Grecbowic J, Chuah H, Lebedev BV, Wunderlich B. J Polym Sci Part B, Polym Phys 1998;36:2499.

[12] Huang J, Chang FC. J Polym Sci Part B, Polym Phys 2000;38:934.

[13] Wu J, Schultz JM, Samon JM, Pangelinan AB, Chauh HH. Polymer 2001;42:7141.

[14] Wu J, Schultz JM, Samon JM, Pangelinan AB, Chauh HH. Polymer 2001;42:7161.

[15] Grebowicz JS, Brown H, Chuah H, Olvera JM, Wasiak A, Sajkiewicz P, Ziabicki A. Polymer 2001;42:7153.

[16] Yang J, Sidoti G, Liu J, Geil PH, Li CY, Cheng SZD. Polymer 2001; 42:7181.

[17] CHO JW, Woo KS. J Polym Sci Part B, Polym Phys 2001;39:1927.

[18] Chuah HH. Polym Engng Sci 2001;41:308.

[19] Bulkin BJ, Lewin M, Kim J. Macromolecules 1987;20:830.

[20] Romano G, Russo R, Vittoria V. J Macromol Sci Phys B 1998;37:841.

[21] Velikov V, Marand H. J Therm Anal 1997;49:375.

[22] Alizadeh A, Richardson L, Xu J, McCarteny S, Marand H, Cheung YM, Chum S. Macromolecules 1999;32:6221.

[23] Bonnet M, Rogausch KD, Petermann J. Colloid Polym Sci 1999;277: 513.

[24] Canadas JC, Diego JA, Mudarra M, Belana J. Polymer 1998;39:2795.

[25] Qian R, Shen D, Sum F, Wu L. Macromol Chem Phys 1996;197:1485.

[26] Montserrat S, Cortes P. J Mater Sci 1995;30:1790.

[27] Verma R, Marand H, Hsiao B. Macromoleules 1996;29:7767.

[28] Bassett DC, Olley RH, Al Raheil AM. Polymer 1988;29:1745.

[29] Lu SX, Cebe P. Polymer 1996;37:4857.

[30] Dean DJ. Thermoplstic Mats 1992;5:136.