Effects of Microcrystallinity and Morphology on Physical Aging and Its Associated Effects on Tensile Mechanical and Environmental Stress Cracking Properties of Poly(ethylene terephthalate)

Hongxia Zhou, Elizabeth A. Lofgren, Saleh A. Jabarin

Polymer Institute, Department of Chemical and Environmental Engineering, College of Engineering, The University of Toledo, Toledo, Ohio 43606-3390

ABSTRACT: Poly(ethylene terephthalate) samples with volume fraction levels of crystallinity up to 27% have been evaluated in terms of physical aging, tensile mechanical properties, and environmental stress cracking failures. Specific enthalpy recovery values were found to correspond with transitions from ductile to brittle modes of tensile mechanical failures, exhibited by samples with each level of crystallinity. For samples exposed to aging temperatures from 45 to 60°C, these critical enthalpies decrease linearly with increased crystallinity. The environmental stress cracking behavior of semicrystalline PET was found to depend on both crystallinity levels and physical aging. Samples with higher levels of crystallinity undergo stress cracking failures at lower critical stresses than their less crystalline counterparts. Physical aging, before environmental stress cracking exposure, further decreases these critical stress values and leads to much shorter critical times for failures. It has been shown that the interspherulitic amorphous portion of the material is primarily responsible for the differences in tensile mechanical and environmental stress cracking behaviors, observed as a result of aging and exposure. This amorphous region becomes progressively more restricted with increasing crystallinity as well as with increased aging. It, therefore, requires shorter exposure times to exhibit brittle tensile mechanical failure and environmental stress cracking rupture. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2906–2917, 2009

Key words: poly(ethylene terephthalate); physical aging; crystallinity; enthalpy of relaxation; tensile mechanical properties; environmental stress cracking

INTRODUCTION

The detailed effects of microcrystallinity and morphology on physical aging of poly(ethylene terephthalate) have been reported previously[1] in terms of specific changes in the relaxation endotherms, observed with differential scanning calorimetry. It was found that overall equilibrium enthalpy of relaxation values decrease linearly with increased crystallinity and with increased aging temperatures. Interspherulitic contributions to the enthalpy of relaxation values were shown to decrease with increased levels of crystallinity, while the intraspherulitic (interlamellar) portions showed corresponding increases. Accompanying these changes, characteristic relaxation times of interspherulitic amorphous regions decreased slightly, whereas intraspherulitic

times increased greatly. Current work seeks to examine the influences of physical aging on the tensile mechanical properties of semicrystalline poly(ethylene terephthalate) (PET). This work also includes examination of the effects of physical aging in terms of environmental stress crack resistance (ESCR) of samples exposed under stress to aqueous sodium hydroxide solutions.

Analyses of mechanical properties are important for materials that require reliability and/or durability during their various applications. Physical aging is a factor known to strongly influence the mechanical properties of polymers[2]; therefore, many attempts have been made to study and predict polymer failure mechanisms. Physical aging is a time dependent behavior of glassy polymers.[3] When such a polymer is quenched from the liquid to a temperature below its glass transition temperature T_g, it has excess free volume, enthalpy, and entropy. As that polymer is stored below its T_g or aged, it will undergo conformational changes as it approaches equilibrium through a process called structural relaxation.[4] Density, enthalpy, and mechanical properties will change during this relaxation process. In

the late 1970s, Struik documented the physical aging effect on creep behavior of amorphous polymers.[3] More recently, other researchers have continued the work to obtain theoretical correlations of volume or enthalpy relaxation with mechanical property changes observed during aging.[5,6]

PET is a widely used engineering plastics which will undergo physical aging when stored below its T_g. Both amorphous and partially crystalline PET can undergo physical aging.[1,3] Mininni[7] reported a correlation between the mode of sample failure and excess free volume by studying amorphous PET. Jabarin and coworkers[8,9] studied PET homopolymer samples and established a relationship between brittle failures and enthalpies of relaxation for both unoriented amorphous and oriented materials. Fewer studies have focused on the effects of physical aging on the mechanical behavior of semicrystalline PET, although Tant and Wilkes[10] investigated variations in the tensile properties of semicrystalline PET upon aging. Their aging temperature, however, was low (23°C), and their data limited to amorphous samples and semicrystalline PET with the levels of crystallinity from 12 to 51%.

The current work has sought to systemically investigate the tensile stress–strain behavior of unoriented PET samples, prepared with levels of crystallinity up to 27%, which were aged at temperatures from 45 to 60°C. The properties studied have been correlated with corresponding relaxation endotherms to elucidate the roles of crystallinity and morphology on these properties.

Environmental stress cracking (ESC) is a time-dependent brittle failure process that proceeds under conditions of long service time and low stress.[11,12] It is caused by environmental factors, such as specific chemical solutions and stresses. ESC includes the aging behavior that results from physical interactions between the polymer material and its environment.[13] It has been estimated that ESC causes from 15–40% of all failures of the plastic components that are in service.[14,15]

The mechanisms of ESC have been the subjects of considerable research. Some researchers[16,17] have proposed that when a sample is under stress, surface defects or morphological inhomogeneities yield high stress concentrations. It is thought that the movement of polymer chains then initiates the formation of small voids and the coalescence of these voids, which is promoted by stress concentration, creates crazes. When a craze thus formed, reaches a critical length, it becomes unstable and grows rapidly until failure occurs. During the ESC process, solutions are thought to act as catalysts during the formation of small voids.[17]

Physical aging is a factor strongly affecting ESC of polymers. Research results indicate that the effects of physical aging are as great as those of some stress-cracking solutions.[8] Longer aging time have been found to delay craze formation; however, once formed these crazes are less stable than those formed at the early stage of exposure.[18]

It has been documented[15,19,20] that variables in a material's structure (including molecular weight, branch length, and lamellar orientation) have great influence on its ESC behavior. In addition, the crystalline content and its distribution with regard to the amorphous phase can also play an important role in the environmental stress crack resistance of a polymer. It has been thought that amorphous plastics could be more susceptible to ESC than semicrystalline plastics because of their lower permeation barrier[14]; however, it has also been found that ESC resistance decreases as crystallinity increases.[21]

The importance of alkaline-induced environmental stress cracking in amorphous PET and on PET/PEN blends has been recognized and studied.[22,23] In the current article, the alkaline induced environmental stress cracking of semicrystalline PET has been studied in terms of tensile creep rupture to clarify the effect of crystalline content on this behavior. The influence of physical aging on ESC was also examined.

EXPERIMENTAL

Evaluations were performed using commercially extruded sheet with thickness values from 0.25 to 0.38 mm. The sheet was prepared from Eastman 9921 PET copolymer, containing 3.5 mol % cyclohexane dimethanol (CHDM), with an intrinsic viscosity of 0.8 dL/g, corresponding to a number average molecular weight (M_n) of 26,000. All samples were exposed to 85°C for 15 min to remove residual stress and previous aging history, before further treatment or evaluation. Samples with the lowest degree of crystallinity 4.6% were not crystallized at 115°C. No spherulites were detected in these materials by small angle light scattering (1); therefore, we have considered this material to be amorphous PET. Various levels of crystallinity were achieved in these samples as a result of controlled, unconstrained, exposure times in a 115°C circulating air oven. Materials prepared at each level of crystallinity were then aged at temperatures of 45, 52, and 60°C in circulating dry air. After the specified aging times, samples to be used for thermal analysis were removed from the oven, cooled to room temperature, and stored in desiccators to maintain dryness. Samples to be used for mechanical testing and environmental stress cracking evaluations were cut into "dog bone" shaped microtensile specimens with gauge lengths of 22.3 mm, 4.75 mm wide at the narrow portion, and thicknesses from 0.25 to 0.38 mm. The aged

samples were then stored at $23 \pm 2°C$ and $50 \pm 5\%$ relative humidity for at least 40 h before evaluation.

An Instron tensile tester, with a crosshead speed of 1.27 cm/min (0.5 in/min), was used to monitor the stress–strain behaviors of samples at room temperature, according to ASTM D 1708 specifications. At least five samples were tested for each measurement, which included yield stress, yield strain, and elongation to break.

The effects of aging samples under environmental stress cracking conditions were monitored at 30°C, in 1000 ppm (0.1%) aqueous sodium hydroxide (NaOH). As described earlier,[8,23] the circulating constant temperature bath used for immersion of samples under stress has upper and lower holders for attachment of samples and lower positioning pins for attaching the lower sample holders at the bottom of the bath. The upper sample holders are fitted to cables which pass over pulleys, transferring forces from adjustable weights to the samples. The apparatus has positions for 10 die cut microtensile specimens. Samples aged under stress are monitored in terms of changes in lengths as functions of exposure times, using linear variable differential transducers and data acquisition software. Strain changes of each sample were recorded every 5 min until all samples were broken. Samples aged before exposures were held in a circulating air oven at 60°C for 3 days.

Sample densities were determined at 25°C using a density gradient column as described earlier.[1] The amorphous copolymer density was taken as 1.323 g/cm^3[24] and that of the 100% crystalline material as 1.455 g/cm^3[25] to calculate the levels of volume fraction sample crystallinity.

Extents of aging were monitored using a Perkin–Elmer (DSC-7) differential scanning calorimeter heated at 10°C per minute. Portions of aged samples were periodically removed and evaluated in terms of their relaxation endotherms as described earlier.[1]

RESULTS AND DISCUSSION

Morphology

Samples prepared for this work were crystallized at 115°C for various times to obtain levels of crystallinity up to 27%. Variations of the degree of crystallinity are shown in Figure 1, plotted as functions of heating time. The three regions indicated in this figure are related to morphological changes that occur in PET during crystallization. According to Keller and Lester,[26] in region I ($X_c < 10\%$), there is very little increase in crystalline content. This is the stage in which crystal nuclei appear in the amorphous material and begin to grow. With increasing crystallization time, percent crystallinity increases in region II ($X_c = 10–20\%$), indicating that the nuclei grow and
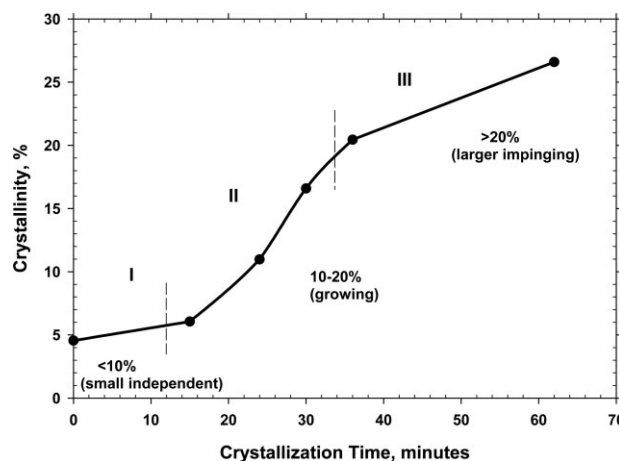
Figure 1 Levels of achieved crystallinity are shown after various exposure times at 115°C.

form spherulites. In region II, spherulitic and amorphous phases coexist. In region III ($X_c > 20$), the rate of crystallinity increases more slowly than in region, indicating the end of primary crystallization and the impingement of spherulites. These regions correspond to changes in the physical aging relaxation endotherms descried in our previous paper concerning the effects of microcrystallinity and morphology on the physical aging behavior of PET.[1] Other researchers[27–30] observed similar phenomena and pointed out that the morphologies of the semicrystalline samples contribute to evidence of double glass transitions representing two different amorphous regions. Their results support our conclusion that the lower temperature relaxation endothermic peaks correspond with amorphous regions between the spherulites, whereas the higher temperature endothermic peaks correspond with amorphous interlamellar regions. Aging has been shown to occur in both of these amorphous regions.[1]

According to the nomenclature described in our previous paper on this topic,[1] an aged sample taken from crystallization region I will exhibit a single lower temperature interspherulitic endotherm described as A_1, whereas an aged sample taken from region II exhibits an endotherm with two peaks. The first is designated as A_1, whereas the second intraspherulitic endotherm peak is A_2. Relative positions of the lower temperature (A_1) interspherulitic and higher temperature (A_2) intraspherulitic relaxation endotherms are illustrated in Figure 8 of our previous paper.[1] An aged sample with region III levels of crystallinity will exhibit a single higher temperature A_2 endotherm. The significance of the A_1 versus A_2 endotherms is that as levels of sample crystallinity increase, lower levels of interspherulitic amorphous materials remain. These interspherulitic materials are the sample portions most responsible

TABLE I
Density, % Crystallinity, and Mechanical Properties of PET Tensile Samples Crystallized at 115°C

Crystallization time (min)	Density (g/cm^3)	X_c (%)	Yield stress (MPa)	Yield strain (%)	Ultimate strain (%)
0	1.3290	4.6	49.0	5.4	355
15	1.3310	6.1	50.8	6.2	368
24	1.3375	11.0	54.5	5.7	351
30	1.3449	16.6	57.4	5.8	339
36	1.3500	20.5	60.3	6.7	332
62	1.3581	26.6	65.9	7.4	341

for changes in polymer properties during mechanical evaluations.

Tensile mechanical evaluations

The mechanical property failure modes of polymer materials are often examined under normal tensile stress at constant strain rates. Under these conditions, polymers generally exhibit either brittle or ductile modes of the tensile failure. Brittle failure occurs at low strain with little or no permanent deformation; whereas ductile failure occurs at high levels of strain.[8,31] In addition to sample properties, the stress–strain behaviors of semicrystalline polymers are dependent on the temperature of measurement as well as the strain rate.[2]

It is generally recognized that the fracture of crystalline tensile samples results from inhomogeneities of morphology.[32] The existence of a crystalline phase reduces the amount of amorphous region that is composed of unfolded chains and restricts the distribution and location of the amorphous phase. This makes samples stiffer and also results in lower ultimate strain values. The tensile mechanical properties of samples prepared at each level of crystallinity were evaluated before aging. An overview of these results is given in Table I, which includes density, % crystallinity, yield stress, yield strain, and ultimate strain or elongation to break (Error levels for average values of at least five tensile specimens are less than 10% for yield stress, 10% for yield strain, and less than 20% for ultimate strain.) Yield strain and ultimate strain are seen to remain relatively constant for these samples, with a slight decrease in ultimate strain for more crystalline samples. Yield stress; however, increased with increasing crystalline content as shown in Figure 2.

Tant and Wilkes[10] evaluated the effects of 23°C physical aging on samples with 0–51% crystallinity. They found that in the first 10 min of their experiments, less % stress relaxation occurred for the samples with higher levels of crystallinity. Increased aging of these samples also resulted in lower % stress relaxation values. These differences were thought to result from the increased glass transition

temperatures, and decreased amorphous fractions that occur with increased crystallinity. Additional factors included variations in local strain in the glassy amorphous regions, increased rigidity of the overall structure, and the decreasing mobility of "amorphous molecules that extend into and become part of" the crystalline fraction. Tensile measurements of their aged samples yielded increases in the Young's modulus and yield stress as well as decreases in the yield strain values. They also recorded changes in enthalpy, supporting the finding that physical aging occurs in semicrystalline as well as in amorphous polymers.

As a result of their findings, selected samples used in the current study were stored at room temperature and evaluated. No embrittlement or significant changes in stress–strain behaviors were observed among these samples, even after they were held at 23°C for more than 100 days. In addition, the measured increases of relaxation enthalpy recorded for these samples were very small. After 107 days, the ΔH value obtained for stored, amorphous PET was 0.5 J/g and values of less than 0.1 J/g were measured for the crystalline samples. These phenomena confirm that in terms of these measurements, the aging process is negligible when the storage temperature is 52° below T_g,[33] as indicated by the WLF (William -Landel- Ferry) equation.[34] For
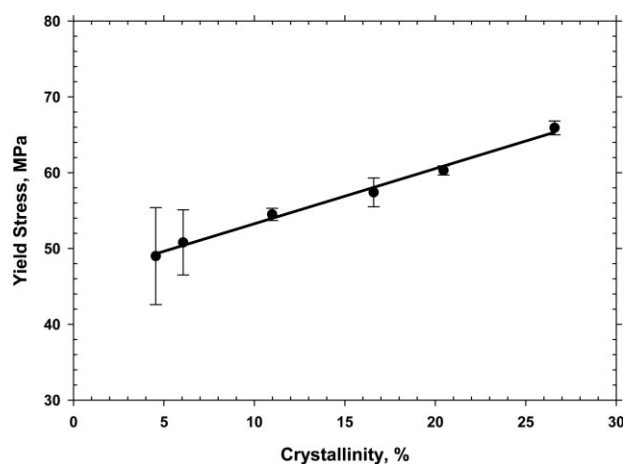

Figure 2 Yield stress values are shown for samples prepared at each level of crystallinity.

TABLE II
Enthalpy and Mechanical Property Changes Resulting from Aging at 45°C

Aging time (days)	Brittle failure (%)	Relaxation enthalpy (J/g)	Yield stress (Mpa)	Yield strain (%)	Ultimate strain (%)
$X_c = 4.6\%$					
0	0	0	49.0	5.4	355
14	0	3.0	56.3	6.6	367
21	0	3.1	54.3	6.0	348
45	0	4.2	51.1	6.3	343
60	0	4.2	53.3	5.7	367
66	0	4.3	56.9	5.5	350
70	20	4.1	57.2	5.6	249
80	0	4.3	54.6	5.4	299
91	0	4.6	52.7	5.6	323
$X_c = 6.1\%$					
0	0	0	50.8	6.2	368
14	0	2.4	57.8	7.0	359
21	0	2.8	54.5	6.1	346
45	0	3.3	57.4	5.6	320
60	20	3.6	54.3	6.5	262
70	40	3.8	60.2	5.9	211
80	0	4.0	54.6	5.4	299
$X_c = 11.0\%$					
0	0	0	54.5	5.7	351
7	0	1.5	55.0	6.0	354
14	0	2.0	57.1	6.3	383
21	0	2.2	59.3	6.0	355
38	0	2.8	57.4	5.9	353
47	0	3.0	55.6	5.5	357
55	20	3.0	59.7	6.2	278
60	20	3.1	57.5	6.8	258
70	60	3.2	62.2	6.1	125
$X_c = 16.6\%$					
0	0	0	57.4	5.8	339
7	0	1.0	61.1	6.5	348
14	0	1.5	59.5	6.0	323
28	0	2.0	60.5	5.8	369
30	0	1.9	–	–	–
38	40	2.1	61.7	6.5	214
50	40	2.3	62.0	6.2	211
60	20	2.4	63.4	6.0	233
80	60	2.6	63.9	6.0	121
$X_c = 20.5\%$					
0	0	0	60.3	6.7	332
7	0	0.9	63.6	6.3	342
10	0	1.1	63.0	6.3	362
14	0	1.1	63.1	6.5	348
21	0	1.2	61.7	6.1	340
28	0	1.4	62.4	6.1	370
30	40	1.7	66.7	6.2	187
50	20	1.8	64.4	6.5	273
60	40	1.8	65.0	6.2	214
$X_c = 26.6\%$					
0	0	0	65.9	7.4	341
1	0	0.1	68.4	6.7	316
2	20	0.2	67.2	6.9	272
7	40	0.4	70.2	6.9	193
10	60	0.5	67.8	6.6	122
28	100	0.9	70.2	6.6	7.1

the amorphous PET tested, $T_g = 76°C$, T_g-52 is 24°C, which is very close to room temperature. This material is, therefore, expected to be stable during room temperature storage. In the case of crystalline PET samples, their T_g values are higher than 76°C; there-fore, it is also reasonable to expect insignificant aging of these materials during room temperature storage.

To obtain more easily the measurable aging effects, portions of the variously crystallized

TABLE III
Enthalpy and Mechanical Property Changes Resulting from Aging at 52°C

Aging time (days)	Brittle failure (%)	Relaxation enthalpy (J/g)	Yield stress (Mpa)	Yield strain (%)	Ultimate strain (%)
$X_c = 4.6\%$					
0	0	0	49.0	5.4	355
9	0	2.9	55.9	5.3	378
14	20	3.6	59.5	5.8	251
18	40	3.8	61.0	5.7	186
21	0	3.8	57.1	5.3	312
31	60	4.2	60.3	6.0	152
42	40	4.5	60.0	6.2	213
$X_c = 6.1\%$					
0	0	0	50.8	6.2	368
9	0	2.6	60.2	5.6	367
12	0	2.9	62.1	5.7	348
14	20	3.0	58.8	5.5	234
18	60	3.2	61.9	5.7	124
31	40	3.8	57.0	5.7	213
42	80	4.1	61.2	6.4	85
$X_c = 11.0\%$					
0	0	0	54.5	5.7	351
7	0	2.0	58.0	5.2	360
11	40	2.2	63.8	5.6	216
14	40	2.6	62.5	5.7	188
18	40	2.8	63.9	5.9	215
31	80	3.1	63.2	6.0	81.1
42	60	3.2	62.8	6.4	158
$X_c = 16.6\%$					
0	0	0	57.4	5.8	339
7	0	1.6	62.0	5.5	341
10	0	1.7	63.3	5.7	353
14	40	2.2	66.8	5.8	218
18	80	2.3	67.1	6.2	75
$X_c = 20.5\%$					
0	0	0	60.3	6.7	332
2.2	0	0.6	65.8	5.7	329
5	0	0.9	62.3	5.3	371
7	40	1.1	68.5	5.8	211
14	0	1.5	59.0	5.4	331
18	80	1.7	69.8	6.2	68
31	20	1.7	67.1	6.1	285
42	40	1.8	65.8	5.9	203
$X_c = 26.6\%$					
0	0	0	65.9	7.4	341
0.5	0	0.1	67.3	6.7	360
0.75	60	0.2	71.1	6.3	153
1	60	0.3	64.7	6.0	138
2	20	0.5	70.4	6.4	267
7	60	–	68.4	7.0	123
14	50	1.0	69.2	6.5	61

materials were aged at temperatures of 45, 52, and 60°C. The tensile mechanical properties of these samples were then monitored after appropriate times of aging. Tables II–IV give overviews of relaxation endotherm values obtained from averages of at least three samples (error levels less than 5%) and corresponding aging times, mechanical property values, and levels of brittle failure. Error levels of less than 10% for average values of yield stress and yield strain are similar to those of the samples before aging; however, error levels of less than 20% for ulti-

mate strain correspond separately to samples breaking in brittle versus ductile modes.

It is known that with aging, the relaxation endotherm and density increase,[3] indicating the increased polymer chain stiffness and the loss of free volume. As a result, samples become brittle. During tensile testing, it is assumed that brittle failure occurs if elongation to break is within 10%. When ultimate strain (elongation to break) values are correlated with the average enthalpies of relaxation measured for the aged semicrystalline samples, inflection

TABLE IV
Enthalpy and Mechanical Property Changes Resulting from Aging at 60°C

Aging time (days)	Brittle failure (%)	Relaxation enthalpy (J/g)	Yield stress (Mpa)	Yield strain (%)	Ultimate strain (%)
$X_c = 4.6\%$					
0	0	0	49.0	5.4	355
1	0	3.1	57.4	5.7	354
2	0	3.5	58.5	6.5	361
2.5	40	3.9	61.9	5.9	217
3	40	4.0	57.4	5.7	216
7	60	4.9	57.4	5.8	147
18	40	5.6	57.8	6.2	215
28	80	5.9	62.1	6.8	81
$X_c = 6.1\%$					
0	0	0	50.8	6.2	368
1	0	2.8	55.0	5.8	368
2	40	3.3	55.8	5.8	235
3	60	3.7	61.8	5.9	136
7	40	4.3	56.2	5.6	225
18	80	5.1	61.0	6.1	71
28	60	5.5	60.5	6.1	134
$X_c = 11.0\%$					
0	0	0	54.5	5.7	351
1	0	2.4	60.5	5.5	378
2	20	2.8	58.1	5.9	289
3	60	3.2	62.2	6.1	144
7	20	3.7	58.2	5.8	249
18	60	4.2	57.2	5.9	148
28	40	4.4	61.6	6.3	203
$X_c = 16.6\%$					
0	0	0	57.4	5.8	339
0.71	0	1.5	64.6	5.7	373
1.25	20	2.1	61.7	5.8	289
3	100	2.5	66.3	6.2	6.3
7	40	2.8	63.8	5.9	203
18	40	3.5	62.2	6.0	198
28	40	3.8	65.5	6.7	213
$X_c = 20.5\%$					
0	0	0	60.3	6.7	332
0.58	0	1.1	66.2	6.0	357
1	60	1.4	69.4	6.4	137
3	80	1.6	67.9	6.3	77.5
7	60	2.2	64.3	5.9	158
18	100	2.7	66.0	6.1	6.3
28	80	2.8	67.5	6.7	67
$X_c = 26.6\%$					
0	0	0	65.9	7.4	341
0.1	0	–	71.6	6.9	326
0.25	20	0.4	70.0	6.8	252
3	100	1.2	69.8	6.6	7
7	80	1.3	69.9	6.5	74
18	60	1.8	66.8	5.7	136
28	100	1.9	72.5	6.6	6.6

points can be observed indicating the onsets of brittle failures. Figure 3 illustrates these transitions from ductile to brittle modes of failure for the various crystallized samples, aged at 60°C. Similar plots were obtained for samples aged at 45 and 52°C. Elongation to break values shown in the tables and figure are the average percent elongations at break of at least five samples.

It has been documented that similar enthalpy-mechanical property relationships occur with amorphous unoriented and oriented PET.[8,9] In this work, the ΔH recorded at the inflection point was called the critical enthalpy required for failure. This means that before this enthalpy value is reached, no samples fail in brittle modes during tensile evaluations. For samples of an unoriented amorphous PET

TABLE V
Density, %Crystallinity, and Activation Energy (E_a)
Values for Onset of Brittleness of PET Tensile Samples
Crystallized at 115°C

Density (g/cm^3)	X_c (%)	Slope (E_a/R)	E_a (kJ/mol)	E_a (kcal/mol)
1.3290	4.6	23,505	195	47
1.3310	6.1	24,046	200	48
1.3375	11.0	23,392	195	47
1.3449	16.6	23,205	193	46
1.3500	20.5	24,015	200	48
1.3581	26.6	14,683	122	29

homopolymer, a critical enthalpy of 3 J/g was reported after exposure to an aging temperature of 40°C. In the current experiments, the critical enthalpy value obtained for amorphous PET copolymer samples aged at 45°C is 4.2 J/g. In the case of similarly aged samples, crystallized to levels of 27%, the corresponding critical enthalpy is only 0.2 J/g. Critical enthalpy values were determined for samples with each level of crystallinity and aged at temperatures of 45, 52, and 60°C. These values are plotted in Figure 4. It can be seen that the critical enthalpy (ΔH) values, required for tensile brittle failure, decrease linearly as the levels of sample crystallinity (X_c %) increase. No significant differences are apparent as a result of the various aging temperatures.

The observed decreases in critical enthalpies required for failure of more highly crystalline samples are consistent with the morphological changes that occur as the degrees of crystallinity are increased in the samples. When more crystals are formed, less amorphous fraction is available and the mobility of this fraction is further restricted by the presence of spherulites or lamellae. The crystalline samples become more compact and inhomogeneous; therefore, the critical point indicating the transition from ductile failure to brittle failure is reached at lower ΔH values. The importance of Figure 4 is that it implies a technique for predicting the mechanical properties of aging samples with the aid of thermal analysis, because an aged sample will not undergo brittle tensile failure until after its critical enthalpy is reached.

Crystallinity and morphology effects

The critical aging time required for brittle tensile failure to occur corresponds to the critical enthalpy. These values are plotted as functions of % crystallinity in Figure 5. At aging temperatures of 45, 52, and 60°C, it is apparent that the times required for brittle failures to occur decrease linearly with increasing

crystallinity. Higher aging temperatures are seen to accelerate the rate of embrittlement. These data were used to calculate the activation energies for embrittlement of samples with each level of crystallinity. According to the Arrhenius equation, ln t was plotted as a function of $1/T$. In this case, t is the critical aging time required for the initiation of brittle tensile failure and T the aging temperature. Table V gives a summary of the slope and activation (E_a) values calculated for samples with each level of crystallinity. It can be seen that samples crystallized up to levels of 20.5% exhibit similar activation energies, near 196 kJ/mol. The sample with 26.6% crystallinity requires 122 kJ/mol for failure.

According to the previous work,[8,9] activation energies of E_a = 136–167 kJ/mol (32.4–40 kcal/mol) were calculated for amorphous PET, consistent with our current noncrystallized sample is E_a = 195 kJ/mol

TABLE VI
ESC Times to Failure at Various Stresses for PET
Samples with Different Crystalline Contents Not Aged
and Aged Before Exposure

| X_c (%)	Not aged			Aged 3 days at 60°C		
	Stress (psi)	Time to failure (h)	S.D.	Stress (psi)	Time to failure (h)	S.D.
4.6	1400	44.0	23.0	180	54.3	49.0
	1500	34.3	13.9	300	27.4	7.7
	1800	29.4	6.0	500	15.7	4.7
	2000	12.8	2.3	800	3.2	1.0
	2300	7.8	1.0	1500	1.6	0.2
	2500	6.6	2.0			
	2800	6.3	1.2			
4.8	1000	42.1	27.3	300	22.7	6.7
	1300	23.4	11.9	500	13.2	7.1
	1500	23.9	9.1	800	4.7	3.1
	1800	13.0	1.8	1500	2.4	1.7
	2000	11.6	3.6			
	2300	6.6	3.3			
10.4	1000	45.1	25.2	300	22.6	21.8
	1300	34.2	17.6	500	11.3	4.5
	1500	22.6	10.7	750	4.7	1.5
	2000	13.1	2.9	1000	2.1	1.3
	2500	7.8	1.6			
	2800	4.9	0.8			
14.6	800	63.7	26.7	180	39.6	27.0
	1300	28.0	11	300	30.5	17.5
	2000	11.9	4.3	500	13.2	13.8
	2500	7.1	4.3	750	3	1.1
	2800	4.2	0.6	1000	2.6	0.3
17.6	1000	42.5	15.8	180	28.8	13.9
	1400	24.2	10.1	300	22.6	14.9
	1800	10.6	5.1	500	7.7	4.8
	2000	9.9	5.3	750	5.0	2.6
	2500	6.2	1.7	1000	5.0	3.2
27.1	500	30.2	19.5	180	21.7	0.6
	700	19.0	14.1	300	11.4	2.8
	900	15.8	6.8	500	8.8	7.1
	1500	9.4	7.0	1000	3.6	2.5
	1800	10.8	11.0			
	2000	7.5	5.5			
	2500	2.4	1.0			
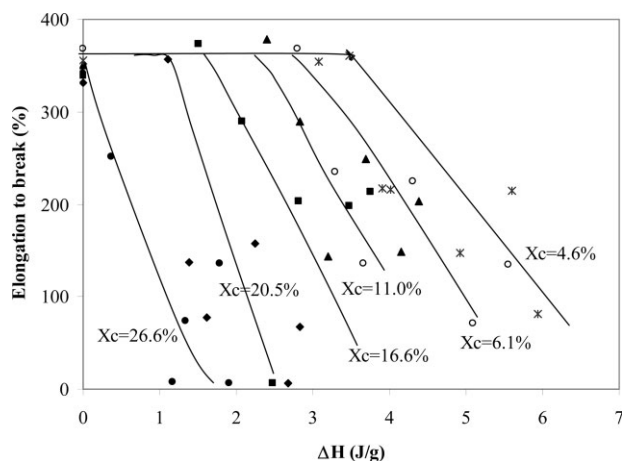
Figure 3 Elongation to break (ultimate strain) values are plotted as functions of their corresponding enthalpies (ΔH), for 60°C aged PET, with levels of crystallinity from 4.6 to 26.6%.

(46.9 kcal/mol). The drop to 122 kJ/mol (29 kcal/mol) at a crystallinity of 26.6% is consistent with morphological changes that occur during crystallization. These results show that when spherulites begin to impinge and levels of crystallinity exceed 21%, as shown in Figure 1, E_a decreases and the samples become more brittle upon aging.

Effects of crystallinity on environmental stress cracking

Past researchers have expressed thoughts that increased levels of crystallinity in unoriented PET samples might impart some protection against environmental stress cracking. This was based on the idea that the more impermeable nature of the crystalline phase could provide an increased barrier to stress cracking solutions.[14] To investigate this possi-
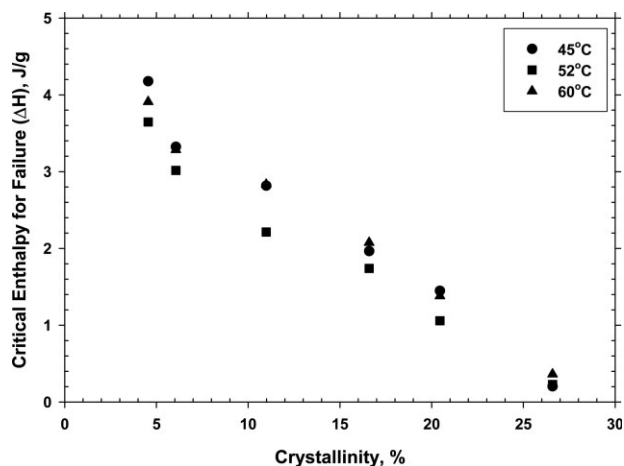
Figure 4 Critical enthalpies (ΔH) required for brittle failures are shown as functions of crystallinity for PET aged at 45, 52, and 60°C.
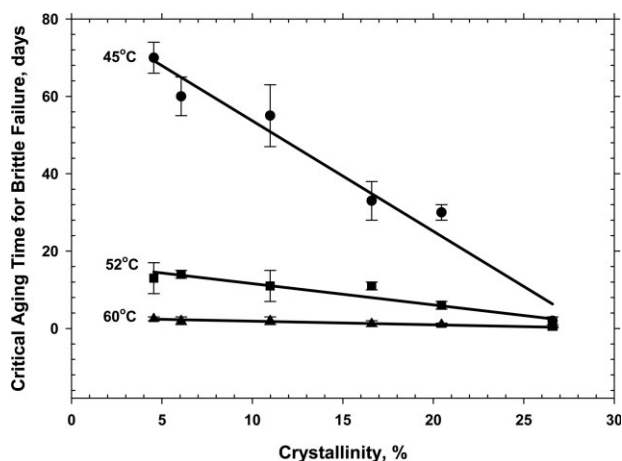

Figure 5 Critical aging times required for brittle failures to occur are plotted as functions of crystallinity for PET aged at 45, 52, and 60°C.

bility, samples of PET with levels of crystallinity from 4.6 to 27% were held under constant tensile stresses and exposed to 1000 ppm (0.1%) aqueous sodium hydroxide solutions at 30°C. Table VI includes average times to failure, obtained for at least five samples exposed at each condition of stress. Figures 6 and 7 include graphic examples of the times to failure plotted as functions of the various levels of stress, for previously unaged samples with mid (10.4%) and higher (27.1%) levels of crystallinity. The relationship between the time to failure and applied stress is seen to exhibit two intersecting trend lines with very different slope values. The point at which the slope changes in each plot indicates the critical stress and critical time to break for samples prepared with each level of crystallinity. Table VII includes a listing of critical stress and critical time to failure values obtained for the previously unaged-exposed samples.
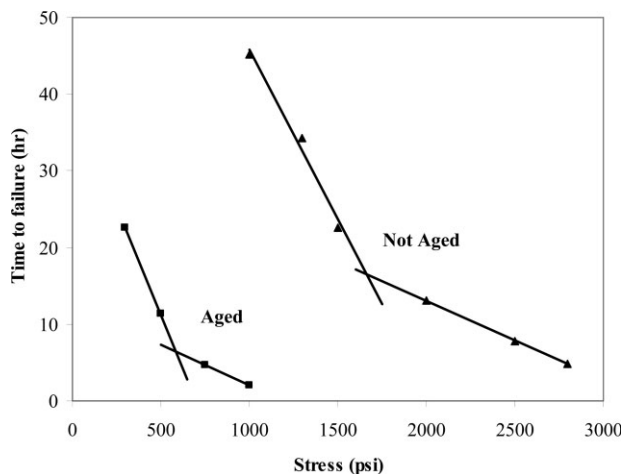

Figure 6 Comparisons of ESC times to failure are plotted as functions of stress levels, for previously unaged and aged PET containing 10.4% crystallinity.
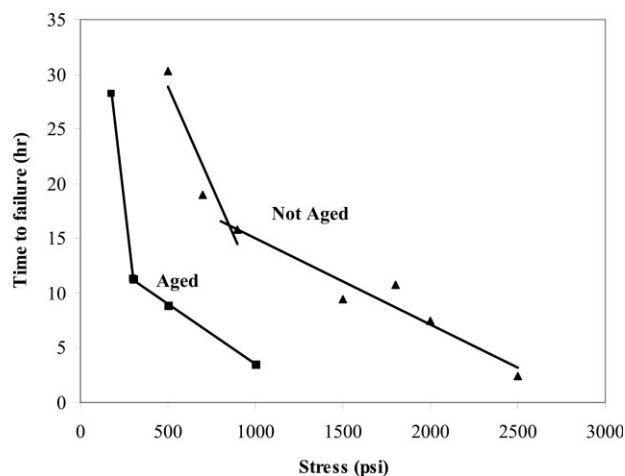
Figure 7 Comparisons of ESC times to failure are plotted as functions of stress levels, for previously unaged and aged PET containing 27.1% crystallinity.

The experimental data included in Table VII indicate that samples with higher levels of crystallinity require lower critical stresses to undergo stress cracking failure than required for less crystalline samples. The critical times recorded at these lower critical stresses, however, are longer. These results can be explained by consideration of a primary mechanism related to the environmental stress cracking of semicrystalline polymers. This mechanism includes the disentanglement or rupture of tie-molecules, which are thought to act as binders, attaching together the adjacent lamellae.[15] According to the mechanism proposed by Lustiger and others,[35,36] when a constant tensile force is applied to a semicrystalline polymer under ESC conditions, the tie molecules (polymer chains) passing through adjacent lamellae are stretched until they cannot pull out further. Over a relatively long period of time, the tie molecules relax and untangle. This finally results in brittle failure. In their research with poly-ethylene pipe samples,[35,36] they observed the fractures to follow a path through the centers of spherulites or through the interspherulitic amorphous regions between them.

The polyethylene samples of Lustiger and others[35,36] were very highly crystalline, whereas the PET samples examined in the current investigations contain less than 30% crystallinity (Levels of crystallinity in PET can be as high as 60%.) Evaluated PET samples cover the crystalline range up to the occurrence of spherulitic impingement. At these levels of crystallinity, very little secondary crystallization has occurred, and considerable amorphous polymer still exists, within and between the spherulites. As has been demonstrated in our previous paper,[1] significantly different aging behavior occurs within these two amorphous phases. Aged, interspherulitic, amorphous materials exhibit decreasing equilibrium enthalpy of relaxation values and shorter characteristic relaxation times, with increasing levels of crystallinity. The amorphous intraspherulitic regions of equivalent samples, however, are found to give increasing equilibrium enthalpy of relaxation values and longer characteristic relaxation times. Tie chain failures, therefore, would be expected to occur within the interspherulitic amorphous regions of the current PET samples. As previously discussed, when crystalline levels increase, there are fewer available tie-molecules to be stretched between the crystalline lamellae. This gives rise to the easier failures observed for the more crystalline samples. This mechanism appears to overcome any advantages gained with the effects of reduced solution permeation.

Physical aging effects on environmental stress cracking

There are many factors affecting ESCR,[14,15] which include stress, temperature, time, cyclic loading, fluid, microstructure, molecular weight, and distribution as well as thermal history. Previous work has shown that physical aging has a great influence on ESCR,[8,18,23] we have, therefore, included investigations of ESC behavior of semicrystalline PET samples aged at 60°C for 3 days before exposure. Results of these additional investigations are given on Table VI. Each average time to failure represents

TABLE VII
Critical Stresses and Critical Times for PET Samples with Different Crystalline Contents Not Aged and Aged Before ESC Exposure

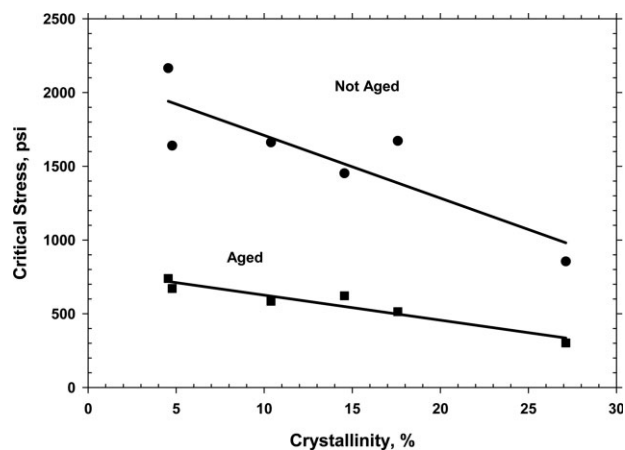| Density (g/cm^3)	X_c (%)	Not aged		Aged 3 days at 60°C	
		Critical stress (psi)	Critical time (h)	Critical stress (psi)	Critical time (h)
1.3290	4.6	2165	8.0	739	3.3
1.3293	4.8	1640	15.5	671	5.1
1.3367	10.4	1662	16.5	585	4.4
1.3422	14.6	1452	17.0	622	3.2
1.3462	17.6	1672	11.7	514	7.2
1.3588	27.1	855	16.1	302	11.2

Figure 8 Relationships of critical stresses to levels of crystallinity are shown for PET samples not aged and aged before ESC exposure.

at least five exposed samples. Figures 6 and 7 show examples of results obtained for previously aged samples with mid and higher levels of crystallinity, in comparison to those for equivalent samples exposed without prior aging. Samples of both types undergo continued physical aging during ESC immersion and evaluations.

It is clear that the plots of times to failure versus stresses shift to lower stress levels and lower ESC exposure times for aged samples. Table VII gives the corresponding critical stress and critical time to failure values. When compared with samples not previously aged, we find that at the same levels of crystallinity, critical stress values decrease dramatically as a result of preaging the samples for 3 days at 60°C. Figure 8 illustrates the relationship of critical stress and levels of sample crystallinity for the 60°C aged samples as well as for those not previously aged. It can be seen that in both cases, critical stresses decrease as levels of crystallinity increase. These results also clearly indicate that previous aging accelerates environmental stress cracking. According to Arnold,[18] aged polymer chains become stiffer and less mobile, delaying craze initiation and growth; however, once crazes are formed they are less stable and make the samples easier to break.

SUMMARY AND CONCLUSIONS

The current work has utilized samples of PET, with levels of crystallinity up to 27%, for investigations of changes in tensile mechanical properties and environmental stress cracking behaviors, especially in relationship to physical aging.

Results of the tensile mechanical evaluations indicate that physical aging of all samples causes ultimate strain (elongation to break) to decrease significantly. In plots of these data, there are inflec-

tion points in terms of corresponding enthalpy values, indicating transitions from mechanical failures in ductile to those in brittle modes. These critical enthalpy (ΔH) values decrease linearly as percent crystallinity increases. Activation energy for embrittlement of samples with levels of crystallinity from 4.6 to 20.5% were near 196 kJ/mol; whereas the value for samples of 26.6% crystallinity was 122 kJ/mol. Samples with higher crystallinity are more brittle indicating that when spherulites begin to impinge, semicrystalline PET is easier to break.

The environmental stress cracking of PET was studied by exposing samples with different crystalline contents to a 30°C, 0.1% aqueous sodium hydroxide solution at various stresses. The ESC behavior of semicrystalline PET was found to depend on both crystallinity levels and physical aging. Results indicate that samples with higher levels of crystallinity undergo stress cracking failures at lower critical stresses than their less crystalline counterparts. Physical aging before environmental stress cracking exposure was found to significantly decrease the critical stresses and lead to much shorter critical times for failure. The critical stresses of both previously unaged and aged samples were found to decreases linearly with increasing crystallinity.

The observed changes in both tensile mechanical and environmental stress cracking behaviors of the evaluated semicrystalline PET samples can be explained in terms of previously reported results.[1] As the samples are aged at temperatures below their glass transitions, overall enthalpy (ΔH) of relaxation values decrease with increasing levels of crystallinity. Their overall characteristic relaxation times increase with increased crystallinity and with decreased aging temperatures. These overall values, however, have been separated into contributions from the more mobile interspherulitic (A_1) amorphous regions and from the more restrained (interlamellar) intraspherulitic (A_2) amorphous regions. These results indicate that the interspherulitic amorphous regions (A_1) give lower equilibrium relaxation endotherm values as levels of sample crystallinity increase, whereas the intraspherulitic amorphous regions (A_2) give correspondingly higher equilibrium relaxation endotherm values. These differences follow changes in distributions of amorphous contents, from outside the spherulites to within them. In addition, it was found that at higher levels of sample crystallinity, characteristic relaxation times obtained for interspherulitic amorphous regions decrease very slightly, whereas those of intraspherulitic amorphous regions increase greatly.

It can be seen from this discussion that as levels of crystallinity increase, overall amorphous content must decrease. The distribution of this amorphous

region is also altered, with increased portions located within the spherulites; while progressively lower levels of amorphous material occupy the A_1 interspherulitic regions. It is this A_1 amorphous material that is primarily responsible for the differences in tensile mechanical and environmental stress cracking behaviors, observed as a result of aging and exposure. The amorphous A_1 region becomes progressively more restricted with increasing crystallinity as well as with increased aging. It, therefore, requires shorter exposure times to exhibit brittle tensile mechanical failure and environmental stress cracking rupture.

References

1. Zhou, H.; Lofgren, E.; Jabarin, S. J Appl Polym Sci 2007, 106, 3435.
2. Browstow, W.; Corneliussen, R. W., Eds. Failure in Plastics; Hanser Publishers: Munich, 1986; pp 98–118.
3. Struik, L. C. E. Physical Aging of Amorphous Polymers and Other Materials; Elsevier: New York, 1978.
4. McKenna, G. B. Comput Mater Sci 1995, 4, 349.
5. Cowie, J. M. G.; Harris, S.; McEwen, I. J. Macromolecules 1998, 31, 2611.
6. Cowie, J. M. G.; Ferguson, R.; Harris, S.; McEwen, I. J. Polymer 1998, 39, 4393.
7. Mininni, R. M.; Moore, R. S.; Flick, J. R.; Petrie, S. E. B. J Macromol Sci Phys 1973, B8, 343.
8. Jabarin, S. A.; Lofgren, E. A. Polym Eng Sci 1992, 32, 146.
9. Mukherjee, S.; Jabarin, S. A. Poly Eng Sci 1995, 35, 1145.
10. Tant, M. R.; Wilkes, G. L. J Appl Poly Sci 1981, 26, 2813.
11. Howard, J. B. SPE J 1959, 15, 397.
12. Howard, J. B. Stress-Cracking, in Engineering Design for Plastics; Baer, E., Ed.; Reinhold Publishing Corporation: New York, 1964; Chapter 11, p 742.
13. Ehrenstein, G. W. Polymer Materials: Structure-Properties-Applications; Hanser Publishers: Munich, 2001.
14. Wright, D. Environmental Stress Cracking of Plastics; Rapra Technology Limited: Shawbury, 1996.
15. Soares, J. B. P.; Abbott, R. F.; Kim, J. D. J Polym Sci Part B: Polym Phys 2000, 38, 1267.
16. Wellinghoff, S.; Baer, E. J Macromol Sci Phys 1975, B11, 367.
17. Arnold, A. J. Trip 1996, 4, 403.
18. Arnold, J. C. Polym Eng Sci 1995, 35, 165.
19. Lustiger, A. In Failure in Plastics; Browstow, W.; Corneliussen, R. D., Eds.; Hanser Publishers: Munich, 1986; Chapter 16, pp 305–329.
20. Fellers, J. F.; Kee, B. F. J Appl Polym Sci 1974, 18, 2355.
21. Howard, J. B.; Martin, W. M. SPE J 1960, 16, 407.
22. Moskala, E. J. Polymer 1998, 39, 675.
23. Jabarin, S. A.; Lofgren, E. A.; Sakumoto, S. In Handbook of Thermoplastic Polyesters, Volume 2: Homopolymers, Copolymers, Blends, and Composites; Fakirov, S., Ed.; Wiley-VCH Verlag Gmb H: Weinheim, 2002; Chapter 22, pp 965–1089.
24. Boyd, T. Effects of Copolymerization on the Heat Set Properties of Poly(ethylene terephthalate), Master's Thesis, Polymer Institute, University of Toledo: Toledo, OH, 1995.
25. Bunn, C. W.; Daubeny, R. P. Proc R Soc London Ser A 1954, 226, 531.
26. Keller, K.; Lester, G. R. Philos Trans R Soc London B Biol Sci 1954, A247, 1.
27. Montserrat, S.; Cortes, P. J Mater Sci 1995, 30, 1790.
28. Diego, J. A. J.; Cañadas, J. C.; Mudarra, M.; Belana, J. Polymer 1999, 40, 5355.
29. Boyer, R. F. J Polym Sci Symp 1975, 50, 189.
30. Groeninckx, G.; Berghmans, H.; Smets, G. J Polym Sci Polym Phys Ed 1976, 14, 591.
31. Birley, A. W.; Haworth, B.; Batchelor, J. Physics of Plastics: Processing, Properties and Materials Engineering, Hanser Publishers: Munich, 1991.
32. Peterlin, A. J Polym Sci Part A-2: Polym Phys 1969, 7, 1151.
33. Foltz, C. R.; McKinney, P. V. J Appl Polym Sci 1969, 13, 2235.
34. Williams, M. L.; Landel, R. F.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.
35. Lustiger, A.; Markham, R. L. Polymer 1983, 24, 1647.
36. Lustiger, A.; Corneliussen, R. D. Mod Plast 1996, 63, 74.