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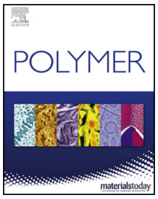

Polymer crystallinity and the ductile to brittle transition

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HIGHLIGHTS

- Organic acid solutions accelerate the molecular weight degradation of polyamide-11.
- Accelerated degradation techniques isolate the role of crystallinity on ductility.
- Crystallinity determines the ductile to brittle phase transition, not chain length.

ABSTRACT

The effects of crystallinity and molecular weight on the ductile-brittle transition of a semi-crystalline polyamide were de-coupled. Low molecular weight organic acid solutions were used to accelerate the molecular weight degradation of polyamide-11 to be faster than with water aging at 120 °C. The mass average molecular weight (M_m) of the aqueous acid aged polyamide-11 (PA-11) polymerized from 11- aminodecanoic acid degraded 4 times faster in acetic and 8 times faster in butanoic acid solutions than aging in water. With accelerated M_m degradation, crystallinity increased due to chemi-crystallizaion but at a slower rate than decreases in molecular weight. These accelerated molecular weight degradation techniques made it possible to separate the role of crystallinity from molecular weight on PA-11 ductility. This research on degradation of a semi-crystalline polyamide in acidic solutions and in water shows that reaching a critical crystallinity determines the ductile to brittle phase transition, not chain length as measured by molecular weight.

1. Introduction

Knowing the molecular basis for the rapid change from a tough, highly, elastic polymer to a brittle material is a very important issue for semi-crystalline polymers. This ductile-brittle transition event occurs as a semi-crystalline polymer ages during use. Understanding at the fundamental molecular level what molecular property is changing and the result on structural performance properties is essential to monitor the polymer material and to determine the safe-use lifetime.

An important use of semi-crystalline polyamide polymers is in the petroleum industry. Here long chain polyamides, such as the semi-crystalline polymer polyamide-11 (PA-11) polymerized from 11-aminodecanoic acid, are widely used for the transport of petroleum in its various forms. A worldwide use is as the liner in deep sea flexible pipes called risers. The PA-11 lined pipes transport crude oil (crude), a complex mixture of hydrocarbons, water and organic acids, from the ocean floor to offshore oil platforms. Trying to understand when and why PA-11 becomes brittle during use in this complex crude–water environment has been the subject of many studies [1–20].

At the molecular level, chain entanglements have been proposed to be the key factor in determining the ductile-brittle behavior of a polymer. For an amorphous linear chain polymer, a critical entanglement chain length, molecular weight, has been characterized [21–24]. This knowledge of how the molecular weight influences polymer embrittlement in amorphous polymers has been extended to linear chain semi-crystalline polymers [17]. In contrast to amorphous polymers, semi-crystalline polymers hold complex relationships between the crystalline domains, chain entanglement, and chain length as measured by molecular weight.

For many years, the molecular weight of semi-crystalline polymers has been proposed as the fundamental molecular property that causes the transition from ductility to brittleness [1,17]. Given the importance of PA-11 risers' safe transport of petroleum, degradation of its performance properties due to changes in molecular properties has been extensively studied [1–20]. Molecular weight, crystallinity, composition of the crude, presence of oxygen, chemicals added to the flowline, and additives in the commercially formulated polyamide are all factors that have been investigated. Among those studies that focused on several of these factors, results based on molecular weight alone have been shown to be imprecise [4–8,12,14,15,18].

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Earlier PA-11 molecular weight studies demonstrated that there is a time during use when, for a given temperature and aging environment, the rate of change in molecular weight reaches an apparent unchanging value. Under those conditions it is hypothesized that an apparent equilibrium molecular weight occurs due to the re-polymerization of unreacted chain ends that effect an increase the molecular weight now becoming equal to the much reduced effect of chain scission. This result has been observed is several experimental studies and predicted in aging models [11,13,17]. In recent years, a focus has been on the factors that affect the apparent equilibrium molecular weight. This is important because if the equilibrium molecular weight can be held above the value associated with the transition to brittleness, extended safe use is predicted.

Previous research has been on the effect of fabrication additives such as plasticizers on the equilibrium molecular weight. The major additive in offshore grade PA-11 is N-n- Butylbenzenesulfonamide (BBSA) [25]. A purpose of BBSA is to disrupt hydrogen bonding and thereby decrease the crystallinity of PA-11. As a plasticizer, BBSA makes PA-11 more ductile and easier to extrude. Studies have shown that BBSA has the added benefit of a higher equilibrium molecular weight during accelerated water aging [3,10,12,20]. The correlated effects that the BBSA plasticizer, crystalline regions, and molecular weight have on the mechanical performance of PA-11 have been recognized and studied by Mazan and Jorgensen [13–15].

Notable among these investigations is the recent investigation by Okamba-Diogo, Richaud, Verdu, Fernagut, Guilment and Fayolle [18] of the changes in crystallinity, morphology and molecular weight of PA-11 during embrittlement. The study examined the relationship between crystallinity and molecular weight on the related decreasing ultimate strain. Oxidation was used to degrade the molecular weight of PA-11 at 110 °C, while stabilizers were used to alter the rate of mass average molecular weight (M_m) degradation. During the course of the study, they observed the transition from relative ductility to brittleness in oxidized PA-11, and ultimately embrittlement of PA-11. Oxidation of stabilized PA-11 took 67 days at 110 °C to reach embrittlement in air, four times the time it took for the un-stabilized PA-11 to encounter the ductile-brittle transition. It was reported that the time to embrittlement for both stabilized and unstabilized PA-11 was coarsely correlated with a molecular weight of 10 kg/mol for both stabilized and unstabilized PA-11. It was discussed in detail how changes in the distance between lamellar crystalline regions tracked the onset of brittleness in PA-11; similar to results in an earlier report on polyethylene [5,18]. As a result of the study, a mixed criterion of the effect of crystallinity and molecular weight on chain embrittlement was developed. A thought is that chain entanglement in the amorphous region is the key to ductility and is determined by the size of the amorphous regions between the crystalline lamellae.

Over the past twenty years a significant factor that influenced the focus on M_m determining the onset of the brittle transition is the American Petroleum Institute's viscosity molecular weight criteria [1]. This focus grew out of early reports on monitoring and modeling the degradation of PA-11's molecular weight in water [11,17]. The 2003 API technical report 17TR2 recommended a method for predicting and avoiding failure of the PA-11 liner by monitoring the molecular weight through the inherent viscosity corrected for concentration of additives (CIV) in offshore commercial P40TLO PA-11 [1]. A corrected inherent viscosity, CIV of 1.05 dL/cm^3 was considered the onset of possible failure in the API technical report. This value was based on field experience. Based on our laboratory data, a CIV = 1.05 dL/cm^3 corresponds to M_m = 32 kg/mol. Thus, a higher CIV value of 1.20 dL/cm^3 was proposed [1] as the time when careful M_m monitoring is needed.

Here our results demonstrate that crystallinity is the fundamental factor that determines the ductile brittle transition. While quite complex as previous work shows, the experimental studies described here focus on decoupling the rate of change of the two principal factors: 1) the molecular weight and 2) the extent of crystallinity. In an effort to separate and identify the separate effects of M_m and crystallinity on ductility, PA-11 samples of the same M_m but different crystallinity were prepared and their ductility was measured. Specimens of the same M_m with different crystallinity was achieved by a much faster rate of change in molecular weight than the change in crystallinity. This objective was accomplished by aging experiments where small organic acids were added to the water [10]. Aging environments with the inclusion of small organic acids found in crude oil causes a more rapid decrease in molecular weight compared to the rate of increase in crystallinity. By aging in weak organic acid solutions the effects of M_m and crystalline content on PA-11's ductility were de-coupled. This paper describes the experimental results that demonstrate that crystallinity detects the onset of the ductile-brittle transition versus the role of the length of polymer chains as measured by M_m.

2. Experimental

Two samples of commercial offshore grade PA-11 extruded from Arkema's Besno P40TLO pellets were used in this study: P1 and P2. The P1 specimens were extruded from Arkema's Besno P40TLO pellets, contained N-n-Butylbenzenesulfonamide (BBSA) plasticizer at 12.5% by weight, had a starting M_m of 110 ± 15 kg/mol, a crystalline content measured at 31 J/g, and an ultimate strain of 592 ± 50%. The measured crystalline content of 31 J/g is considered to be a 16% crystallinity where the 100% crystallinity heat of fusion (ΔH_{fus}) for PA-11 is taken to be 189 J/g [26], P2 specimens were extruded from Arkema's Besno P40TLO pellets, had 12.5 wt% BBSA, a starting M_m of 89 ± 9 kg/mol, a crystallinity of 35 J/g or 19%, and an ultimate strain of 372 ± 35%.

Both P1 and P2 were formed into dogbone tensile test specimens with an active length of 3 cm. The thickness of P1 was 2 ± 0.5 mm compared to P2, 0.3 ± 0.02 mm. Mechanical tests were performed on an 810 Material Test System at a rate of 6.35 mm/min; the stroke was used to measure the relative strain. The PA-11 dogbones were immersed in deionized water, acetic, or butanoic acid solution, each acid concentration was at $6.3 \times 10^{-2} M$, and aged at 120 °C over a period of 8, 2, and 1 months respectively to accelerate aging and M_m degradation. Ace #40 high pressure rated glass tubes with Teflon™ plugs were used as containment vessels. Before sealing the pressure tube, oxygen was removed by sparging the aqueous solution with argon in-situ to achieve a concentration below 50 ppm to avoid oxidative degradation, as measured with an Oakton DO + 6 dissolved oxygen meter.

A TA Instruments Q20 Differential Scanning Calorimeter (DSC) was used to measure the crystalline content of PA-11. A ramp rate of 3 °C/min was used to heat the samples under nitrogen from 40 to 220 °C with peak integration limits of 140–200 °C. The measured ΔH_{fus} values had an error margin of 5% as determined by the standard deviation divided by the mean for consecutive measurements on a single sample.

A TA instruments Thermal Gravimetric Analyzer 500 (TGA) instrument was used to determine the water and plasticizing molecule content of the aged PA-11 in each aging environment using a 5 °C/min ramp with a 30-min 100 °C hold, then ramp up to a final 90-min hold at 250 °C.

Multiple in-line size exclusion chromatography (SEC) columns (Shodex HFIP-LG, HFIP-805, and HFIP-803) with a Wyatt miniDAWN multi-angle laser light scattering (MALLS) detector and Wyatt Optilab 803 dynamic refractive index detector were used to measure M_m. The details of these measurements have been published [10]. The measured M_m values have an error margin of 6% as determined by the standard deviation divided by the mean for consecutive measurements on a single solution of PA-11.

3. Results and discussion

Low molecular weight acids accelerated the hydrolysis aging of PA-11, as shown in Fig. 1. A direct comparison can be made between the

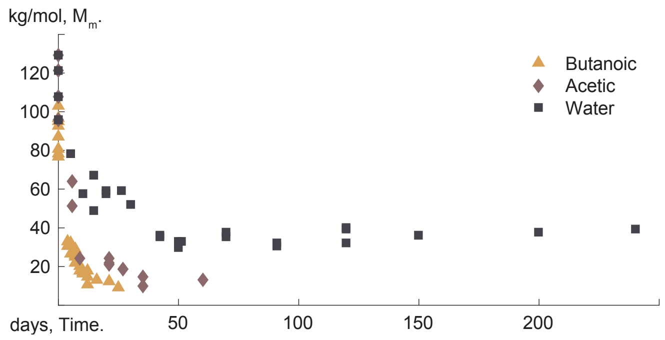

Fig. 1. PA-11 M_m versus time correlated to the accelerated aging environment.

water aged and acetic acid aged conditions as both sets of data were taken using the same P1 starting material. The rate of change in M_m was strongly affected by the organic acid solution aging environments, as Hocker, Rhudy, Ginsburg and Kranbuehl [10] previously reported. PA-11 samples aged in acetic acid solution at 120 °C degraded from 110 kg/mol to 22 kg/mol in 21 days, a rate of 4.2 kg/mol/Day. Acetic acid aged samples reached an approximate equilibrium M_m of 13 kg/mol after 35 days. Conversely, PA-11 samples aged in deionized water at 120 °C reached an equilibrium M_m of 36 kg/mol in 42 days, a rate of 1.76 kg/mol/Day. PA-11 samples aged in butanoic acid solution at 120 °C degraded from a M_m of 89 ± 9 kg/mol to 25 kg/mol in 7 days, a rate of 9.1 kg/mol/Day. Although the P2 samples have a lower starting molecular weight, it is relevant that the butanoic environment accelerated the M_m degradation down to 19 kg/mol in 9 days, 7.8 kg/mol/day - whereas it took 27 days for the acetic aged samples to drop the M_m down to 19 kg/mol, 3.4 kg/mol/day – butanoic aged more than twice as fast as the acetic acid environment. Butanoic acid aged samples did not reach an equilibrium, but did record a minimum M_m of 9 kg/mol after 25 days.

Table 1 reports the ultimate strain of the aged PA-11 samples at varying molecular weights. Fig. 2 displays the absence of any correlation of molecular weight with ductility as measured by ultimate strain. Fig. 2 shows PA-11 samples of both P1 and P2, aged respectively, with the same M_m and different ultimate strains as a result of the aging environment, i.e. rate of acceleration. PA-11 samples aged in both acetic and butanoic acid solution maintained ductile behavior at M_m in the range of 30 ± 5 kg/mol. Butanoic aged samples after 4 and 5 days aging showed 395% and 367% ultimate strain at 33 kg/mol and 32 kg/mol respectively. Comparatively, water aged samples aged 50–240 days exhibited M_m from approximately 30-40 kg/mol and ultimate strain values of 75–116%. PA-11 samples aged in both acetic acid and butanoic acid solutions remained ductile well into the 20 kg/mol range. PA-11 aged in acetic acid for 27 days had a M_m of 19 kg/mol exhibited an ultimate strain of 249%. PA-11 aged in butanoic acid 7 days had M_m from 22 to 29 kg/mol and ultimate strain values from 304 to 359%. This shows that ductile behavior was achieved at M_m far below the equilibrium molecular weight of PA-11 aged in DI water (approximately 36 kg/mol), and that M_m was not the molecular factor that determined the ductile-brittle transition.

Increases in the crystalline content as measured by ΔH_{fus} are reported Fig. 3 and Table 1. The increase was due to crystallization by the shorter more mobile chain fragments as chain scission proceeds. Fig. 2 and Table 1 also report the macroscopic mechanical property of interest: ultimate strain. It decreases with decreasing M_m over time and with the increase in crystallinity. Table 1 shows that for water aged PA-11 the ductility decreased over 240 days as it achieved an equilibrium M_m. The decrease in ductility followed closely with the increasing crystallinity with time due to annealing during most of this time.

Table 1
Time, mass average molecular weight, heat of fusion, and % ultimate strain: for samples aged in butanoic solution, acetic solution and water.

Day	M_m (kg/mol)	ΔH (J/g)	Ultimate Strain (%)
Butanoic Acid Aged			
0	77, 97, 81, 78, 93, 95, 103, 87	35	331, 355, 333, 388, 380, 359, 461, 413, 369, 357, 347, 404, 368, 345
4	31, 33	39	258, 395, 312, 337, 393
5	27, 32	47	294, 367, 336
7	25, 26, 22, 29	51, 49, 52	304, 346, 316, 359
9	18, 20	65	179, 180, 129
10	18, 16, 17	56, 55, 63	146, 147, 92
12	15, 11, 18	61, 62, 62	133, 117, 101
16	13	69	17, 20, 17
21	12	72, 67	9, 8, 9, 10, 11, 10
25	9	65	1
Acetic Acid Aged			
0	129, 121, 96, 108, 96	31	573, 583, 665, 548
6	64, 51	40	473
9	24	48	388
21	21, 22, 24	63, 58, 60	371
27	19, 19	58	249
35	15, 10	70, 72	28
60	13	74	1
Water Aged			
0	129, 121, 96, 108, 96	31	573, 583, 665, 548
5	78	49	248
10	58	51	320
15	49, 67	48	235
20	58, 59	63, 59	216
26	59	59	301
30	52	58	339
42	35, 36	66	212
50	30, 33	67	98
51	33	72	116
70	35, 38	68	107
91	31, 32	73, 76	90
120	39, 32,40	76	81
150	36	77	80
200	38	80	83
240	39	81	75

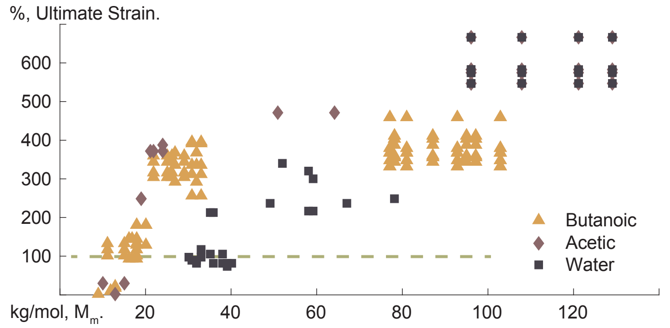

Fig. 2. PA-11 samples % ultimate strain persus kg/mol M_m correlated to accelerated aging environment at 120 °C. The dotted line indicates the herein defined brittle regime at 100% ultimate strain and below.

The acetic acid aged PA-11 achieved a much lower equilibrium molecular weight of about 18 kg/mol compared to about 36 kg/mol for water. Once at the equilibrium M_m, the increased crystallization through thermal annealing again caused a decrease in ultimate strain.

For butanoic acid aged PA-11, at a molecular weight as low as 17 kg/mol, the butanoic aged PA-11 was ductile, and had an average 128% ultimate strain, with a ΔH_{fus} of 58 J/g. The PA-11 aged in butanoic acid became brittle before an equilibrium molecular weight could be reached.

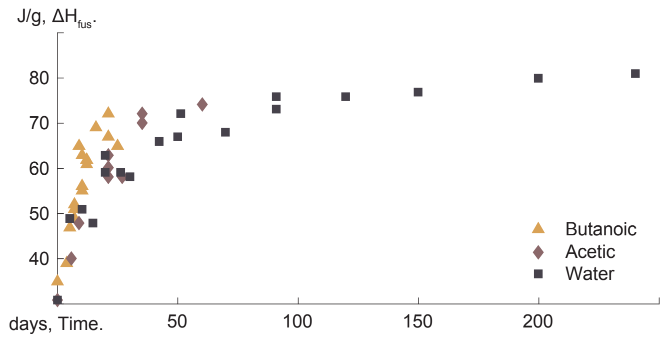

Fig. 3. PA-11 samples' J/g ΔH_{fus} versus time in days.

Overall, Figs. 2 and 3 show that the PA-11's crystallinity strongly affects the polymer's ductility. In the acid solutions, when the crystallinity was low, at a ΔH_{fus} below approximately 60 J/g and at a M_m below 20 kg/mol, PA-11 remained ductile. Conversely in DI water, when the M_m was 38 kg/mol with $\Delta H_{fus} = 68$ J/g, PA-11 was entering the ductile brittle phase transition having an ultimate strain of 107%. Herein an ultimate strain of 100% or less was taken to be the brittle regime. Once water aged PA-11 was at the equilibrium M_m at 120 °C, the brittleness of the PA-11 progressed gradually with increases in crystallinity due to annealing.

Prior to achieving an equilibrium M_m, Table 1 and Fig. 3 show a rapid increase in crystallinity and decrease in ductility, Fig. 5. This is due to the degraded polymer chain fragments and their mobility. The crystalline content increased rapidly, chemi-crystalization, relative to increases in crystallinity due to annealing when at an equilibrium M_m. Table 1 and Figs. 2 and 3 show that crystalline content determined the point at which PA-11 underwent the ductile to brittle transition. With increasing crystallinity, the molecular volume for chain entanglements in the amorphous regions was reduced. A reduction in molecular volume for chain entanglement is a molecular morphological basis for the effect of crystallinity on ultimate strain-ductility and helps explain why crystalline content determined the point at which PA-11 underwent the ductile to brittle transition.

The acid accelerated experimental approach isolated the correlated effect of a critical crystallinity and the previously proposed critical molecular weight on embrittlement. The results show for semi-crystalline PA-11 that there was a critical embrittlement ΔH_{fus} of 67 J/g, or 35% crystalline content, the lowest measured crystalinity of all the brittle samples. We offer that an experimental critical ΔH_{fus} embrittlement value can be used to model and monitor the strain behavior of PA-11 as well as other semi-crystalline polymers, and to determine point where further decreases in ductility are unacceptable.

Conceptually, under different molecular weight degradation conditions relative to increases in crystallinity, there may be a low critical molecular weight coupled with a low crystallinity that causes embrittlement. This possibility was not observed here.

Fig. 4 displays ΔH_{fus} vs M_m. During chemi-crystallization there appears to be a linear relationship of a changing molecular weight and increases in ΔH_{fus}. The relationship of chemi-crystallization during degradation in M_m and a resulting lamellar thickening has been previously shown [4,18]. While it was previously accepted that the onset of the ductile to brittle transition tracked with molecular weight, now having created distinctly different rates for degradation it can be seen that the ductile to brittle transition tracks with crystallinity. A reason for the previous use of molecular weight to monitor changes in ultimate strain was the similarity in increases in crystallinity to decreases in molecular weight during accelerated high temperature aging in water [1,17].

Figs. 4 and 5 water aged square symbols show the ductile to brittle transition occurred at the same degree of crystallinity through the chemi-crystallization process in butanoic and in acetic solutions as during the approach to an equilibrium M_m for water aged PA-11. The chemi-crystallization process occurred as the more mobile shortened polymer chains and fragments aligned more quickly, while migrating to and onto the thickening lamellar regions. The slower thermal annealing occurred for the water aged equilibrium M_m, where the temperature determined the molecular mobility.

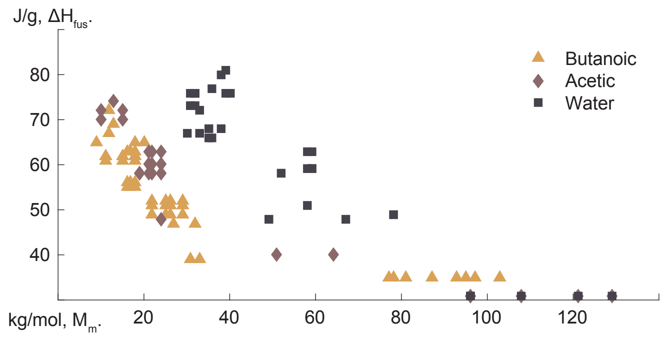

Fig. 4. PA-11 samples' J/g ΔH_{fus} (crystallinity) versus kg/mol M_m correlated to acid accelerated versus water aging environments at 120 °C.

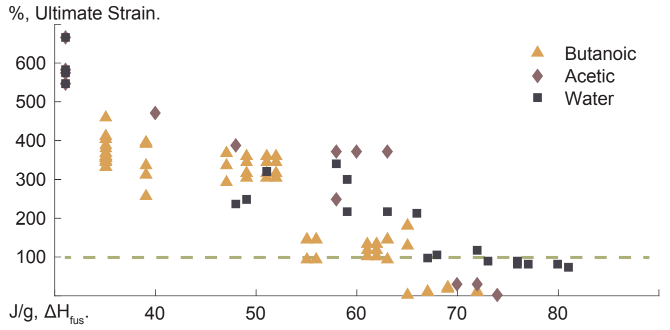

Fig. 5. Ultimate strain versus heat of fusion, showing the brittle cut-off at 100% ultimate strain as the dashed line.

After the initial decrease in M_m and increase in the crystallinity, the water aged samples spent extended time, 189 days, at the equilibrium M_m. This resulted in the slower annealing increase of the ΔH_{fus} with a decrease in the ultimate strain from 116% to 75% for a total reduction of 41%. When both water and acid accelerated aged PA-11 samples had a ΔH_{fus} of 67 J/g or greater, regardless of the crystallization process, they were in the brittle regime. Thus, at a ΔH_{fus} of 67 J/g brittleness was expected regardless of molecular weight.

Fig. 5 and Table 1 indicate the onset of the transition from ductility to brittleness began with a ΔH_{fus} in the range of 55–60 J/g, and brittleness occurred at 67 J/g. The relationship of crystallinity to ductility as discussed agrees with earlier results on oxidative aging of polyethylene and PA-11 [5,18]. Here it was reported that the onset of embrittlement was correlated to the distance between crystalline regions using small angle X-ray diffraction [18]. This molecular distance is also clearly a measure of the space available for chain entanglements and related to the increases in crystalline content as measured by heat of fusion.

Plasticizers added to polyamides and small molecules in the aging environments that diffuse in to polyamides are known to increase the polymer's elasticity and decrease the melting temperature. In the user guide for Arkema, the 12.5% plasticized commercial PA-11 Besno P40TLO is reported to have an average ultimate strain of 380% while the unplasticized PA-11 Besno TL has an ultimate strain of 360%. Thus for the commercial polyamide 11, the effect of 12.5% of the plasticizer was to increase the elongation at break by 20% or a little over 5% in magnitude [27]. The role of BBSA is to disrupt and reduce crystalline content. Previous aging studies have shown that small organic acids accelerate PA-11 hydrolysis because of their solubility and diffusivity into PA-11. As a result the small organic acids, diluted in water, diffuse into the polymer at varying amounts depending on the temperature, concentration, and solubility characteristics [10]. In PA-11 aged to molecular weights below 40 kg/mol, the TGA weight loss measurements showed the small molecule content to be 6% in pH7 water, 12% in acetic solution, and 11% in butanoic solution. It is likely that the effect of the additional plasticizer mixture of BBSA and the small organic acid has a modest effect of around 5% or less in magnitude on ultimate strain: based on the effect of 12.5% BSSA in commercial PA-11. It can be hypothesized from these TGA results that the 5% higher concentration of BBSA and small acid plasticizing molecules in the acid aged samples contributed to their slightly lower ΔH_{fus} at embrittlement compared with the water aged samples along with the modest effect on the ultimate strain.

In summary, Table 1 shows that the values of the ultimate strain from 300% to 600% decreased as the crystallinity increased. For aging in neutral water, the first time the ultimate strain fell below 100% was at the approximate equilibrium M_m of 36 kg/mol when the ΔH_{fus} was 67 J/g. With increased time the M_m remained constant, the ΔH_{fus} increased and the ultimate strain continued to slowly decrease. For aging in an acetic acid solution, the M_m decreased to 19 kg/mol, the ΔH_{fus} was 58 J/g, and a ductile ultimate strain of 249% was measured; and then the M_m decreased to 13 kg/mol, the ΔH_{fus} increased to 71 J/g, and the ultimate strain dropped to a brittle 28%. For the very rapid aging in butanoic acid, when the M_m decreased to 15 kg/mol, the ΔH_{fus} was 62 J/g and the ultimate strain averaged 117%. When the M_m changed slightly to 13 kg/mol and the ΔH_{fus} increased to 69 J/g, the ultimate strain averaged 18%, 82 points below 100%. Equally important, Table 1 reports differing ultimate strain values at different crystallinities given the same M_m. Taken together, the results demonstrated that brittleness, as defined by an ultimate strain of 100%, for semi-crystalline PA-11 occurred over a wide range in M_m and at or beyond a crystallinity 35% as measured by a ΔH_{fus} value of 67 J/g. These results show that the crystalline content is the fundamental molecular parameter that leads to embrittlement and thereby ΔH_{fus} effectively monitors the decreasing ultimate strain.

4. Conclusions

Small organic acid solution hydrolysis of semi-crystalline PA-11 accelerated the degradation of the mass average molecular weight. The M_m of the acid aged PA-11 degraded 4 times faster in acetic and 8 times faster in butanoic acid solutions than in water. With accelerated molecular weight degradation, crystallinity increased through chemi-crystallization but at a slower rate than the very rapid decrease in M_m. By accelerating the M_m degradation, the challenge of measuring the ultimate strain of semi-crystalline PA-11 material of similar M_m but different crystallinity was overcome. The resulting data was able to separate the effect of changes in crystallinity from molecular weight on the changing ductility and on predicting embrittlement of semi-crystalline PA-11.

This research on acid solution aged and water aged PA-11 shows that increases in crystallinity results in a decrease in ductility. Reaching a critical crystallinity in PA-11 as measured by a heat of fusion of 67 J/g determines the onset of the ductile to brittle phase transition, not chain length as measured by molecular weight. Rather chain scission plays a secondary role in that it enables increased chemi-crystallization that increases the crystallinity. Conceptually, the predominance of the effect of crystallinity on ductility over molecular weight should extend to modeling and predicting the ductility of other semi-crystalline polymers analogous to PA-11.

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