Interfacial Tension Measurements and Evidence of Order in High-Density Polyethylene Melts

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ABSTRACT: Polyethylene (PE) is a widely used product commercially. However, our knowledge is incomplete about the properties of high-density polyethylene (HDPE) at temperatures above its melting point, where solid crystals disappear. Recently, there has been increasing evidence from rheological, differential scanning calorimetry, and NMR studies that suggests the presence of microstructural order in the bulk of PE melts. In this study, the interfacial tension of HDPE melts in contact with silicone oil was measured with a spinning drop tensiometer in the same temperature range in which phase transitions have been observed in the bulk HDPE. Anomalous temperature dependence of interfacial tension was found between 200 and 230°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 4061–4067, 2003

Key words: interfaces; interfacial tension; melt; microstructure; polyethylene (PE)

INTRODUCTION

It is conventionally believed that above the melting temperature (T_m) of 135–140°C, high-density polyethylene (HDPE) undergoes a change from the semicrystalline to a melt amorphous phase with no long-range molecular order, that is, a classical random coil.[1] However, there is increasing evidence from rheological, differential scanning calorimetry (DSC), and NMR studies that suggests the presence of microstructural order in the bulk of polyethylene (PE) melts.[2–6] The objective of the research presented in this article was to investigate further the existence of these so-called ordered phases in the PE melts by the examination of the interfacial tension of PE melts at high temperatures. In particular, evidence of microstructural transitions occurring for the melts in bulk have been reported and were taken to imply changes in the nature of molecular order. Controversy about these results in the bulk properties encouraged us to seek also transitions in the interfacial properties.

Despite the importance of polymer melt interfacial tension in polymer blending processes, little data and information are available in the literature on the dependence of the interfacial tension of polymer melts on temperature.[7–9] This can most likely be attributed to experimental difficulties, such as the long equilibration time for the polymer and the high temperatures involved.[8] Among the limited data available on the interfacial tension of PE melts, few data points are available for temperatures as high as 240°C, and most experiments were conducted with large temperature steps, for example, with a measurement made every 10°C.[9–15]

Due to the lack of data points, it is sometimes difficult to ascertain whether the interfacial tension data over a wide temperature range should be represented by a monotonic linear function or whether the scatter in the data indicates a noncontinuous curve. Because the conventional belief is that PE melts behave like an isotropic liquid (with interfacial tension decreasing monotonically with increasing temperature), linear monotonic functions have always been used to describe the data. As a result, some experimentalists have overlooked some anomalous observations in their measurements of the interfacial tension of PE melts at high temperatures. Pham and Carriere[12] measured the interfacial tension of polycarbonate/PE with the imbedded-fiber retraction method from 210 to 240°C, where a peak was observed at 220°C. However, due to the large standard deviation associated with the measurement at that temperature, the authors fit a linear regression line through all of the data points and offered no explanation for the observed peak. Rao[16] measured the interfacial tension of polypropylene and linear low-density polyethylene at 200, 220, and 260°C with the breaking thread method. A peak in the interfacial tension was observed at 220°C. The author suggested that the peak was likely due to a different experimental procedure applied for the measurements at 220°C but could not point out the specific cause of the observed peak.

Carriere et al.[9] measured the temperature dependence of the interfacial tension of polystyrene (PS)/poly (methyl methacrylate) (PMMA), PS/PE, and PMMA/PE with the imbedded-fiber retraction method. For these studies, the temperature ranged from 140 to 220°C. For the PS/PE system, a peak in the interfacial tension was observed at 180°C, which was similar to the observation of Pham and Carriere.[12] For the PMMA/PE system, a discontinuity in the interfacial tension was also observed at 200°C. However, a peak was not observed for the PS/PMMA pair. Again, due to the large standard deviation associated with the measurement at that temperature, the authors fitted a linear regression line through all of the data points and offered no explanation for the observed peak or the discontinuity with the two systems that contained PE.

In the present study, the interfacial tensions of HDPE melts were measured with a spinning drop tensiometer obtained from SDT, Ltd. (University of Minnesota, Minneapolis, MN). The spinning drop method was chosen because of the flexibility and ease with which the experiments can be conducted in a continuous manner at high temperatures. The results presented in this article comprise the most comprehensive interfacial tension study of HDPE to date, with more than 15 data points measured over the range 160–250°C. We show that discontinuities do exist in the interfacial tension–temperature curve, and thus, the anomalies observed by previous experimentalists were not due to experimental error. Rather, these surface tension discontinuities are consistent with the anomalies observed in other rheological, NMR, and DSC studies.

EXPERIMENTAL

Materials

For the measurement of the interfacial tension of the silicone oil/PE pair with spinning drop tensiometer, the PE melt was the less dense fluid, and silicone oil was the denser fluid over the whole temperature range. Silicone oil was chosen as the denser medium for several reasons. First, silicone oil is known to be an isotropic fluid. As such, during the measurement of the interfacial tension of PE/silicone oil, any property anomalies observed would be due to PE alone and would not be contributed to by the silicone oil. Second, silicone oil is denser than the PE, thus allowing easier loading of the samples into the spinning drop tensiometer than the solid–solid loading typically used for polymer interfacial tension measurements. Third, silicone oil (Fluid 710, Dow Corning Co., Midland, MI) is heat-stabilized at high temperatures, with upper temperature limits of 260°C for open systems and 315°C for closed systems. Finally, previous experiments by Hussein[17] showed that silicone oil did not

TABLE I
Properties of the HDPE Investigated

PE producer and product code	ρ at 25°C (g/cm^3)	M_n	M_w	M_w/M_n	M_z
HDPE Exxon 6750	0.951	10,823	35,946	3.32	79,871

M_n = number-average molecular weight; M_w = weight-average molecular weight; M_z = z-average molecular weight.

diffuse into the polymer in the temperature range of 200–230°C, thus ensuring that the silicone oil would be an inert medium contacting the PE. Oil from two different cans were used for the different experiments in the work, and we found that the two oils had different viscosities and densities. These two cans of silicone oil were likely different batches of the same product. In this article, silicone oil A and B are used to differentiate the two different batches of oil.

The PE used to investigate the possible phase transitions at the interface at high temperatures was a commercial HDPE of rather low molecular weight, preferable for the spinning drop experiment because of its low viscosity. It was obtained originally in pellet form, with each pellet approximately 0.03 cm^3 at room temperature. The properties of this HDPE are shown in Table I. The molecular weight distribution and averages were obtained by gel permeation chromatography (GPC) in our department.[17]

Methods

Measurement of the interfacial tension of silicone oil and the PE melt

The interfacial tension of PE and silicone oil was measured with a spinning drop tensiometer. The operation of the spinning drop tensiometer is based on the theory derived by Vonnegut.[24] When a drop of fluid is enclosed in a container filled with an immiscible denser fluid and subjected to high rotation rates with respect to the horizontal axis, the less dense fluid will migrate to the axis of rotation and elongate to assume a cylindrical shape with hemispherical ends.[24] The measurement of the cylinder radius yields the calculated value of interfacial tension, which is a function of the rotation rate, density of the fluids, and radius of the drop.[25] Details of the spinning drop principle may be found in Vonnegut's article.[24] A detailed description of the spinning drop tensiometer used for this work, including the error analysis of the apparatus may be found elsewhere.[23] With care, measurements with an error of only ±3% were obtained for the spinning drop tensiometer used in this work. The interfacial tension of HDPE in contact with silicone oil was measured from 180 to 250°C with temperature

increments of 10°C (and 5°C over the temperature range of greatest interest). Each set of experiments was conducted at a constant rotation rate.[20] A small temperature increment was chosen so that any anomalous variation in the interfacial tension of the PE melt would be captured.

Silicone oil was loaded first into the glass tube at room temperature. Two PE solid pellets were then placed inside the glass tube filled with the silicone oil, also at room temperature. The glass tube filled with silicone oil and PE pellets was then loaded on the spinning drop tensiometer, and the samples were simultaneously rotated and heated to 180°C. The two pellets then merged in the melt state to form one drop of appropriate volume. The first measurement of the interfacial tension of silicone oil in contact with HDPE melt was made once the drop formed an equilibrium cylindrical shape at a constant rotation rate and temperature. Once the measurement was made at the desired temperature, the temperature of the apparatus was then increased by a temperature increment of 5 or 10°C.

Degradation of PE and the blending of antioxidants (AOs) into HDPE

The total time required for each of the interfacial tension experiments (spanning the range 160–260°C) was approximately 2.5 h. Over such a long period of time and at such high temperatures, the HDPE samples showed signs of degradation, that is, browning of the originally white specimen. In an attempt to reduce or prevent degradation, various amounts of AOs (described later) were blended with the HDPE samples before the commencement of the interfacial tension experiments. A Haake Rheocord 90 batch melt blender (Paramus, NJ) was used to blend the AOs into the HDPE. As recommended by Ciba-Geigy Inc. (Tarrytown, NY), the AO used in all of the experiments was a 1:1 blend of Irganox 1010 {Phenol B, tetrakis[methylene 3-(3′,5′-di-t-butylphenol) propionate] methane; weight-average molecular weight $[M_w]$ = 1178} and Irgafos 168 [P-1, tris(2,4-di-t-butylphenol) phosphite; M_w = 646]. The concentrations of the AOs added varied from 1000 to 20,000 ppm. For the blending process, the HDPE and added AOs were initially heated up to 150°C, blended at 50 rpm for 10 min, and then quenched to room temperature before they were used for the interfacial tension experiment. The HDPE with AO, however, was not subjected to the Rheocord conditioning and mixing process.

Densities of HDPE and silicone oil for the calculation of the interfacial tension of the polymer melts

The density for HDPE used for the calculation of the interfacial tension of PE in this study was a monoton-
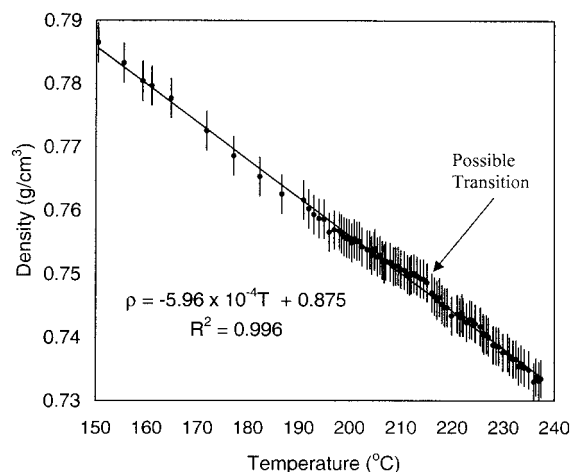

Figure 1 Density of a HDPE specimen between 150 and 240°C. The error bar on each data point is 0.5%.

ically decreasing function of temperature. The densities of the HDPE in the temperature range 180–250°C were obtained with a densitometer similar to that in the ASTM D 792 method.[20] A typical result is shown in Figure 1. The density experiment exhibited evidence of a small anomaly between 200 and 230°C; however, the anomaly was within the experimental error and too small to affect the calculated interfacial tension. As such, a straight line was fitted through the data points, and a linear relationship between HDPE density and temperature was used for the calculation of interfacial tension between HDPE and silicone oil.

The density (ρ) of silicone oil A and silicone oil B were as follows:

$$\text{Silicone oil A: } \rho(\text{g/cm}^3) = 0.9811 - 8.34 \times 10^{-4}T \text{ [17]}$$
$$(1)$$

$$\text{Silicone oil B: } \rho(\text{g/cm}^3) = 1.116 - 6.68 \times 10^{-4}T \text{ [20]}$$
$$(2)$$

where T is the temperature in degrees Celsius. Equations (1) and (2) were valid up to 260°C.

The corresponding relationship used for HDPE was:

$$\text{HDPE: } \rho(\text{g/cm}^3) = 0.875 - 5.96 \times 10^{-4}T \text{ [20]} \quad (3)$$

RESULTS AND DISCUSSION

Interfacial tensions of HDPE without additional antioxidant

We made six sets of measurements (with six different specimens of HDPE) of interfacial tension as a function of temperature by varying the temperature from 160 to 250°C while keeping the rotation rate constant.[23] Three sets of measurements were conducted at
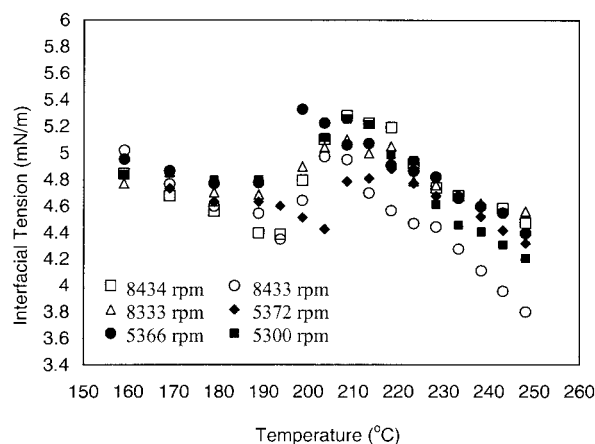
Figure 2 Interfacial tension of Exxon 6750 HDPE (no additional AO) and silicone oil A from 150 to 250°C. A total of six experiments are shown in this graph. The filled data points indicate experiments conducted at a rotation rate of about 5300 rpm, whereas the open data points indicate experiments conducted at 8300 rpm. Errors are not shown for clarity. Calculated errors were ±3%, which was exceeded by the scatter.

a rotation rate of approximately 5300 rpm, and three sets were conducted at 8400 rpm. Silicone oil A was used in these experiments. For temperatures lower than 190°C, a measurement was made every 10°C, whereas at temperatures higher than 190°C, a measurement was made every 5°C. The results for all six runs, as shown in Figure 2, revealed that the interfacial tension of HDPE/silicone oil A was not a monotonic function of temperature. For temperatures lower than 200°C, the interfacial tension (γ) of HDPE/silicone oil decreased linearly as temperature increased. The average $d\gamma/dT$ for all six runs in the temperature range 160–200°C was 0.012 mN/m/°C. This temperature coefficient agreed well with the data collected by Wu,[10] where the $d\gamma/dT$ for most polymer pairs was on the order of 0.01 mN/m/°C.[10] A near discontinuity in the interfacial tension was observed for all six runs between 200 and 230°C, where the interfacial tensions jumped sharply upward with increasing temperature. After reaching the highest value, interfacial tension again became a decreasing function of temperature. Interestingly, although the measured sets of the interfacial tensions of PE/silicone oil were similar at temperatures lower than 200°C, each of the six experiments yielded different transition behaviors between 200 and 230°C; that is, the peak in the interfacial tension occurred at slightly different temperatures. Moreover, after the transition temperatures, some runs exhibited a larger $d\gamma/dT$ than others, and the curves did not overlay one another.

The total time for each set of experiments was approximately 2.5 h. After each experiment, browning was observed for all of the HDPE samples. An additional experiment was conducted to test whether or not the silicone oil degraded under the experimental conditions, thus causing the browning observed in the HDPE samples. A tube filled with silicone oil (without HDPE pellets) was subjected to the same rotation rate, temperature increments, and experimental time described for the HDPE/silicone oil experiments in a spinning drop tensiometer. At the end of this experiment, no discoloration of the silicone oil was observed.

Also, at the end of each HDPE/silicone oil experiment ($T = 250$°C), the HDPE drops became very rigid, such that when the rotation rates of the samples were increased or decreased, the drop diameters did not change. (Rigidity was not observed in the first hour of the experiment.) This rigidity may have been due to the crosslinking of the HDPE molecules, an additional indication that thermal degradation altered the physical properties of the HDPE.

Interfacial tensions of HDPE with additional AO

Additional AO was blended with the Exxon HDPE in an attempt to reduce or prevent the degradation of the polymer sample during the interfacial tension experiment. The interfacial tensions of HDPE with varying amounts of extra AO (7,000, 10,000, and 20,000 ppm) in contact with silicone oil were measured over a temperature range of 190–250°C with a temperature step of 10°C. This smaller temperature range and larger step size were chosen to reduce the experimentation time so that thermal degradation could be minimized. For the 7,000-ppm AO experiment, interfacial tensions for all three runs were not linear functions of temperature, as shown in Figure 3. A discontinuity in the interfacial tension was observed for all of the experiments. However, the discontinuity occurred at different temperatures: 200, 220, and 240°C. For the 10,000-ppm AO experiment, interfacial tensions were
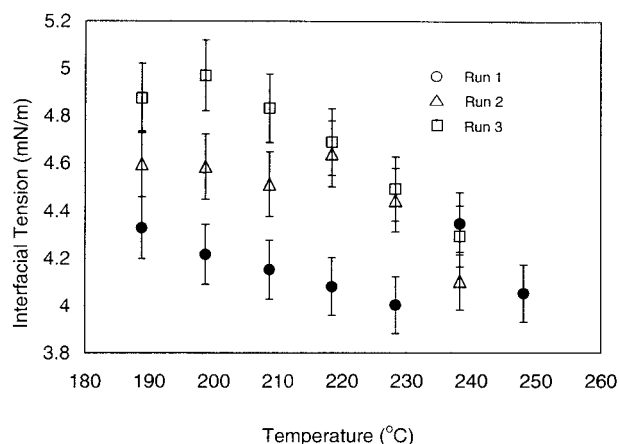

Figure 3 Interfacial tension of Exxon 6750 HDPE with the addition of 7,000 ppm AO in contact with silicone oil A from 190 to 250°C. A measurement was made every 10°C. Runs 1, 2, and 3 were made under identical conditions.
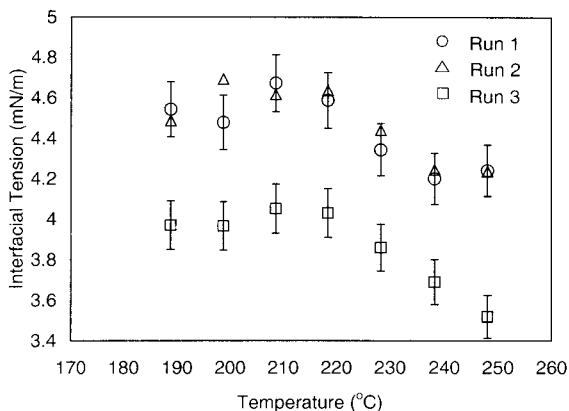
Figure 4 Interfacial tension of Exxon 6750 HDPE with the addition of 10,000 ppm AO in contact with silicone oil A from 190 to 250°C. A measurement was made every 10°C.

again not linear functions of temperature, as shown in Figure 4. Unlike the 7,000-ppm AO experiments, a peak in the interfacial tension was observed in the same temperature range of 210–220°C for all three sets of experiments with another possible anomaly for runs 1 and 2 at about 240°C.

The total experiment times for the 7,000- and 10,000-ppm AO experiments was approximately 1.5 h, which was less than the previously described experiments, for which no additional AO was added. However, browning was still observed for all of the samples after each experiment. The HDPE samples with additional AOs were less rigid at the end of the experiments than the HDPE without additional AOs; unlike the HDPE without additional AOs, the diameter of the HDPE drops with additional AOs changed with ease when the rotation rate of the samples was changed at the end of the experiments. These results indicate that although degradation was not prevented even with the shorter experimentation time and additional AOs (because browning was still observed for all of the samples), according to the rigidity observations, the degradation of the HDPE samples was reduced for the 7,000- and the 10,000-ppm AO experiments. (The amounts of AO used in this work were much higher than the amount that is usually blended in HDPE and what was originally in the HDPE. The amounts of 7,000, 10,000, and 20,000 ppm were added in an attempt to examine the effect of AOs on HDPE degradation reduction.)

The 20,000-ppm AO experiment was conducted with silicone oil B, and the results for the two sets of experiments with 20,000 ppm extra AO clearly showed discontinuities in the temperature coefficients of interfacial tension between 200 and 220°C, as shown in Figure 5(a,b). Browning was still observed for the samples after each of the experiments, and similar to the 7,000- and 10,000-ppm experiments, the diameter of the HDPE drop changed easily with a change in the

rotation rate at the end of each experiment. As such, it appeared that the addition of 20,000 ppm AO did not further reduce the degradation observed with the 7,000 and 10,000-ppm AO experiments.

The interfacial tensions of the HDPE with 20,000 ppm AO added shown in Figure 5 were in the range 2.4–3.4 mN/m between 190 and 250°C, which were lower than the interfacial tensions shown in Figures 2–4. These lower interfacial tension values were most likely due to the difference in the properties of silicone oil used (B vs. A) and also to the addition of large amounts of AO.

Discontinuities in the temperature coefficients of interfacial tensions were observed in all of the HDPE experiments. The interfacial tensions of the PE melt before the transition temperature (160–200°C) linearly decreased with temperature, which has been a common observation for amorphous polymers by other workers. The temperature coefficients in this temperature range were on the order of 0.01 mN/m°C, which is in agreement with published data by Wu.[10] How-
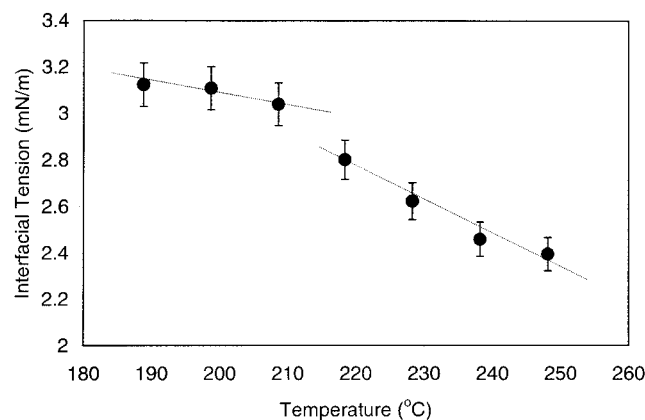
(a)
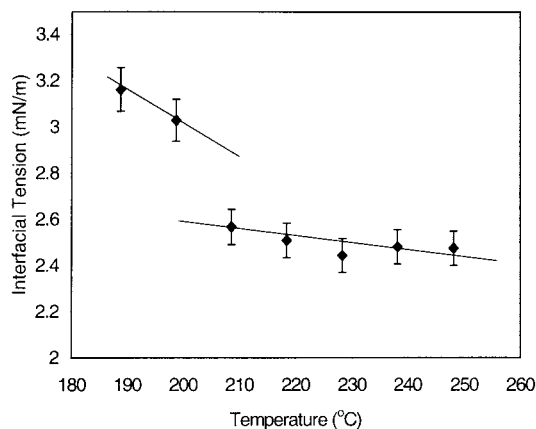
(b)

Figure 5 Interfacial tension of Exxon 6750 HDPE with the addition of 20,000 ppm in contact with silicone oil B from 190 to 250°C. A measurement was made every 10°C: runs (a) 1 and (b) 2.

ever, unlike most amorphous polymers, discontinuities or peaks in the interfacial tension as a function of temperature were observed for all of the HDPE samples. The temperature at which a peak was observed (~220°C) in the interfacial tension was also in close proximity with interfacial tension data of Pham and Carriere,[12] Rao,[16] and Carriere et al,[9] all of whom used different apparatus than was used in this study. Due to the limited number of data points collected, these authors did not comment on this phenomenon and did not provide an explanation of the observed peak; rather, they fitted a $\gamma(T)$ linear regression line through the data points by assigning a large standard deviation to the particular data point, which obviously did not lie in the path of a linear function. From our study, the results shown in Figure 2 clearly show that in the transitional temperature range 200–230°C, the interfacial tension of HDPE without additional AO increased with increasing temperature, and once it reached a maximum, the interfacial tension then decreased with increasing temperature. This was consistently observed for all six runs and was supported by many data points in the transition temperature range. Previous studies of thermooxidative degradation of PE (as detected rheologically) found that corresponding molecular weight changes, as measured by GPC, were usually not statistically significant,[26] so we believe it unlikely that such changes could explain the observed surface tension transitions. These sets of data represent the most comprehensive study of the interfacial tension of PE melts to date, and we have shown that the transition/peak seen in Figures 2–5 and the results of Pham and Carriere,[12] Rao,[16] and Carriere et al.[9] were not due to experimental errors.

The temperature range at which the discontinuities in the interfacial tension–temperature relationship were observed is consistent with the observations of Hussein and Williams,[2,3] who also saw a transition in the rheological and thermal properties of the HDPE in the temperature range 200–230°C. This transition temperature was also consistent with an observed transition in the densities of the HDPE discussed earlier. However, the density used in the calculations of interfacial tension in this study was taken as a smoothed linear function of temperature and, thus, was not a mathematical cause of the $\gamma(T)$ discontinuity reported here.

Hussein and Williams[2,3] suggested that the thermal transitions observed in the HDPE melts are analogous to the transition observed for liquid crystal polymers, and hence, PE melts may exhibit structural order similar to that of liquid crystal polymers. The idea of structural order was also supported by the results published by Kruger et al.,[18] Kamel and Charlesby,[5] and Bremner and Rudin.[19] The results seen in Figures 2–5 also support the speculations of Hussein and Williams. The thermal transition in the interfacial tension

resembled that of order transitions in liquid crystals. The interfacial tensions of liquid crystals (e.g., those with smectic or nematic structural order) undergo thermal transitions from an ordered anisotropic phase to a disordered isotropic phase once the transition temperature has been reached.[20-22] In the pretransition state, interfacial tension increases with increasing temperature. Near the transition temperature, interfacial tension also increases with increasing temperature but with a much greater slope until a maximum is reached. After the transition temperature, interfacial tension then becomes a monotonically decreasing function of temperature. One or more peaks in the interfacial tension are sometimes observed for these liquid crystals.

When the surface behavior of HDPE was compared to that of liquid crystals, the interfacial tension–temperature relationship in the pretransitional temperature range seen in Figures 2–5 was different than that for the liquid crystals,[22] however, the behavior of the interfacial tension at the transition temperature was similar to that of liquid crystals. Kamel and Charlesby[5] and Bremner and Rudin[19] found that three components exist in a PE melt: an ordered component, a disordered but entangled component, and an unentangled component. As such, the decrease in interfacial tension with increasing temperature at the pretransitional state for the PE may have been due to the contribution of the disordered components in the PE melt, whereas the sudden peak observed in the interfacial tension may have been due to a transition in the ordered component in the PE melt.

For the HDPE experiments, the temperature at which the transition was observed was different for each set of experiments, even though most of the transition temperatures lay in the range 200–230°C. Moreover, the transitions observed in HDPE with additional AO (Figures 3–5) were less pronounced than the transitions observed for the HDPE with no additional AOs added. These observations may have been due to differences in the thermal history of the samples, which may have affected the transition behavior. Bremner and Rudin[19] found evidence of ordered material in the PE melt, and the volume fractions of the ordered material largely depended on the particular polymer and its thermal history. The thermal history of the HDPE blended with AO was different than the HDPE with no extra AO as described in the Methods section.

CONCLUSIONS

In the research reported here, we achieved two objectives:

1. As a result of the experimental ease associated with the spinning drop technique used, many

data points were obtained in a wide temperature range. These results represent the most comprehensive study of the interfacial tension of PE melts to date.

2. Thermal transitions in the interfacial tensions between 200 and 230°C were observed for the HDPE (with and without extra AOs) in contact with silicone oil. The characteristics of the transition in interfacial tension for the HDPE were somewhat analogous to those of liquid crystals, and this is consistent with the findings of Hussein and Williams[2,3] and suggests the possible existence of an ordered state in the PE melt. Variations in the transition temperatures were observed for the different sets of experiments, which may have been due to differences in the thermal histories of the polymers.

There remain some questions that can be addressed in future work by us or by others:

1. How is T_m influenced by the addition of extra AO, and could a T_m-shift be responsible for the interfacial tension transitions near 230°C and the apparent density discontinuity there too? We doubt that solid-state crystals with such a high T_m could exist at such a high temperature, and even if AO shifted the T_m slightly upward, that would have given a interfacial tension transition at just above 140°C, which was not seen here (nor in our extensive earlier work with HDPE).

2. Would the $\gamma(T)$ results for samples with and without extra AO agree more closely if those samples had exactly the same thermomechanical history (e.g., suppose the samples without extra AO were sheared in the blender to the same extent as samples sheared during the AO mixing process)?

3. To what extent does the extra AO function as a nucleating agent in the PE as it cools from the blending operation, and could this have an effect on the sample at much higher temperatures?

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