<http://www.diva-portal.org>

This is the final author version of a paper published in *Polymers*.

Citation for the original published paper (version of record):

Yu J., Sundqvist B., Tonpheng B., Andersson O. (2014) Thermal conductivity of highly crystallized polyethylene. *Polymer* 55, 195-200.

<http://dx.doi.org/10.1016/j.polymer.2013.12.001>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:umu:diva-86333>

Thermal conductivity of highly crystallized polyethylene

Junchun Yu, Bertil Sundqvist, Bounphanh Tonpheng, and Ove Andersson*

Department of Physics, Umeå University, 901 87 Umeå, Sweden

* Corresponding author.

E-mail address: ove.andersson@physics.umu.se (O. Andersson).

Tel.: +46 90 7865034; fax: +46 90 7866673.

ABSTRACT

We report thermal conductivity (κ) of low-density, high-density and ultra-high density polyethylene (PE) with different crystallinity and microstructures. PE was crystallized under high-pressure and high-temperature conditions which produce extended chain crystals. By applying a two-phase model, we estimate κ of 100% crystallized PE as a function of pressure and temperature. The increased crystallinity and lamellar thickness (fold length) reduce the thermal resistance, which is reflected not only in the absolute value of κ but also in more pronounced pressure and temperature dependencies approaching those of polycrystalline low-molecular weight materials. The results suggest that it is crucial to increase the lamellar thickness to significantly improve κ of PE with randomly oriented lamellae.

Keywords: Polyethylene, Thermal conductivity, Crystallinity

1. INTRODUCTION

Polyethylene (PE) is the most widely used polymer in various packaging and functional applications, with an annual production of 80 M tons in 2007 [1, 2]. PE consists of $-\text{CH}_2-\text{CH}_2-$ units where the methylene main chain may fold and form crystalline domains, which produces a semicrystalline structure with roughly equal parts of crystalline and amorphous domains. More specifically, the degree of crystallinity depends on the molecular weight (M_w) of PE, which determines both the level of crystallinity and the density. This provides a classification of PE into low-density PE (LDPE, M_w : ~ 50000), high-density PE (HDPE, M_w : ~ 200000) and ultra-high molecular weight PE (UHPE, M_w : ~ 3500000 to 7500000) [2]. LDPE shows a high level of long-chain branching that partially obstructs folding and alignment and gives a crystallinity of typically 40-50% [3]. HDPE and UHPE have linear main chains that promotes alignment and, thus, normally higher initial crystallinities of, respectively, 60-80% and 37-75% [2].

High pressure treatment is a highly effective method to modify the crystallinity of semicrystalline polymers, as shown recently for nylon-6 [4]. High pressure treatment is probably also the best method to produce extended chain crystal (ECC) structures in bulk PE, which was first observed by Wunderlich and co-workers [2]. They defined an ECC as a crystal with fully extended chains (fully ECC), or one with only a few chain folds and a fold length exceeding 200 nm. In a series of studies, Wunderlich and co-workers [5-7] investigated pressure treated PEs and reported lamellae thicknesses up to several microns.

As depicted in the phase diagram of Fig. 1a, PE can adopt two different crystal structures; an orthorhombic phase, which is stable at low pressures and temperatures, and a high pressure, high temperature hexagonal phase, which is stable above a triple point at

0.36 GPa and 483 K [2]. Basset and Turner [8] attributed the efficient growth of ECCs under pressure to a two-stage crystallization via the intermediate hexagonal phase. This provides an explanation for the significant difference in microstructure between PE samples crystallized, or annealed, under pressure and those crystallized directly into the ambient orthorhombic phase, which shows fold lengths, or lamellar thicknesses, of ~ 20 nm [9, 10].

The crystallinity of a polymer affects many of its important properties such as the thermal conductivity (κ). Knowledge of thermal conductivity is essential for, e.g., technological applications and processing of polymers [11]. Several studies of PE [12-14] have concerned the changes in κ of samples modified by uniaxial stretching. This produces PE fibers with highly oriented chains, and κ may increase from ~ 1 to as much as $\sim 100 \text{ W m}^{-1} \text{ K}^{-1}$ because of increased crystallinity and alignment of the polymer chains along the drawing direction [13]. Quite a few studies have also investigated the effect of crystallinity on κ of bulk PE [11], but none of these seems to have addressed the effect of simultaneously increased crystallinity and fold length.

In this paper, we present results of κ of PE (LD-, HD- and UHPE) with different crystallinities, and under pressure. After high pressure crystallization, UHPE reaches a crystallinity of 68% and the temperature and pressure behavior of κ become similar to that of a typical polycrystalline material, which indicate that phonon-phonon scattering is dominant in bulk UHPE with ECCs. By assuming a two-phase model, we estimate κ of polycrystalline and amorphous bulk PE as a function of both pressure and temperature.

2. EXPERIMENTAL SECTION

2.1 Materials

Low density polyethylene (LDPE) and High-density polyethylene (HDPE) with molecular weights (M_w) of, respectively, 50000 and 125000, and in the form of pellets, were purchased from Scientific Products, Inc., SP². Ultra-high molecular weight polyethylene (UHPE) with an M_w in the range 3000000 to 6000000, and in the form of powder, was purchased from Sigma-Aldrich. All the materials were used without further purification.

2.2 Sample preparation and hotwire measurements

The pellet or powder samples were cast into plates for measurements of κ . The original samples were melted at 150 °C (LDPE), 150 °C (HDPE), or 170 °C (UHPE) in a vacuum oven and hot cast in a piston-cylinder device, applying a slight pressure (ca. 0.9 MPa). The cast samples, with a diameter of ~37 mm and a thickness of ~6 mm, were assembled together with a hot-wire sensor into a custom-made Teflon cell. Subsequently, the cell was loaded into a piston-cylinder device and the whole assembly was transferred into a hydraulic press, which delivered the load. We were able to measure κ of the samples for pressures up to 1.5 GPa in the temperature range 100 to 500 K. The inaccuracy in κ is estimated as $\pm 2\%$. The high pressure apparatus and the method of have previously been described in detail [4, 15]. UHPE was also studied by differential thermal analysis (DTA) at 0.5 GPa by heating at an average rate of ca. 0.5 K/min from room temperature to ca. 550 K, and then cooling at ca. 0.5 K/min. (The thermocouples for DTA were inserted in the sample and the Teflon cell wall.) The samples were thereafter recovered at 1 atm for wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) analyses.

2.3 High pressure and high temperature (HP&HT) treatment

The cast plate-like PE samples were loaded in the Teflon cell containing a type K thermocouple. The cell was mounted into a piston cylinder apparatus and the assembly transferred to a press. In a typical HP&HT treatment, the PE sample was treated for 4 h at 535 K and 0.5 GPa. The pressure inaccuracy is estimated as ± 40 MPa at 1 GPa. The pressure and temperature were controlled using two proportional-integral-derivative (PID) controllers, which kept the pressure and temperature constant to within ± 1 MPa and ± 1 K during the 4 h HP&HT treatments.

3. RESULTS AND DISCUSSION

In this work, PE was treated at 0.5 GPa and 535 K during 4 h (HP&HT treatment) to obtain a highly crystallized sample. The sample was first pressurized to 0.5 GPa at room temperature, followed by heating to 535 K and subsequent annealing, as indicated by the dashed arrow in Fig. 1a. Thus, PE was treated in the stable range of the hexagonal phase to produce lamellae with significantly increased fold length, and then cooled isobarically down to room temperature.

Table 1. Crystallinity of various PE samples obtained from DSC measurement (C_{DSC}) and WAXD (C_{WAXD}) before and after HP&HT treatment. Empirical functions for thermal conductivity data in the 150-330 K range at 1 atm (in SI-units): $\kappa = a/T + b + cT$ (UHPE) and $\kappa = a/T + b + cT^5$ (LDPE/HDPE).

Sample	C_{DSC}^a (%)	C_{WAXD} (%)	a	b	c
LDPE	30.6	52.1	-8.16	0.442	-2.15E-14
Treated LDPE	37.5	54.7	-	-	-
HDPE	55.2	52.7	18.2	0.410	-2.06E-14
Treated HDPE	68.2	73.1	28.8	0.433	-2.24E-14
UHPE	46.0	59.0	5.01	0.648	-0.8E-3
Treated UHPE ^b	68.3	79.3	56.3	0.800	-1.3E-3

^aThe values of C_{DSC} are probably more reliable than C_{WAXD} because of better repeatability and because the calculation of C_{WAXD} was less rigorous due to the somewhat arbitrary subtraction of the background.

^bTypical lamellar thicknesses in the 100-150 nm range.

As presented in Table 1, after the HP&HT treatment, DSC results show increased crystallinity C_{DSC} , from 46.0% to 68.3% for UHPE and from 55.2% to 68.2% for HDPE. LDPE, however, showed only a slight increase from 30.6% to 37.5%, which is consistent with its short and branched main chain.

The thermal conductivity (κ) of the PE samples was measured on pressurization at 298 K both before and after HP&HT treatment. As shown in Fig. 1b, κ for LDPE, HDPE and UHPE increase almost linearly with pressure before treatment although there is a weak gradual decrease of the slope in all cases. This is particularly obvious for LDPE. The

decrease is likely due to a decreasing compressibility, and this effect is commonly observed for both crystalline and amorphous solids, especially the latter, unless a phase transition occurs in the range of pressurization.

Values of κ at atmospheric pressure and room temperature were obtained by short extrapolations of the high-pressure results. (Loss of thermal contact between the probe and sample may occur when measurements are done at 1 atm [4].) This yielded 0.367, 0.427 and 0.422 W m⁻¹ K⁻¹ for, respectively, LDPE, HDPE and UHPE. The higher values for the latter two are consistent with their higher molecular weights and crystallinities compared to LDPE (Table 1). After the HP&HT treatment, κ of UHPE increased to 0.579 W m⁻¹ K⁻¹ at 1 atm and room temperature, which gives an increase of 37%. The same result for HDPE is 0.475 W m⁻¹ K⁻¹, or an 11% increase. The significantly larger increase for UHPE than HDPE seems not to be fully explained by the changes in crystallinities, which are of similar magnitude (Table 1). As described below, we instead attribute the main difference in the results to growth of ECCs in UHPE. The results for LDPE before and after treatment differed by only 3.5%.

Fig. 1. (a). Phase diagram of PE from ref 2. The dashed arrows show the path of the HP&HT treatment. (b). Thermal conductivity of PE samples on pressurization at 298 K before ($\square$, LDPE; $\circ$, HDPE; Δ , UHPE) and after (black line, LDPE; $\bullet$, HDPE; $\blacktriangle$, UHPE) HP&HT treatment.

The most interesting result shown in Fig. 1b is the strong and slightly increasing pressure dependence of κ for treated UHPE. This behavior is most unusual for polymers, for which κ versus pressure normally levels off at high pressure. At 1.5 GPa, κ of the treated UHPE was $1.668 \text{ W m}^{-1} \text{ K}^{-1}$, or 68% higher than that of pristine UHPE. This means that the increase is almost twice that at 1 atm (37%), which is due to the stronger pressure induced increase of κ for the treated sample. Several features affect the change of κ for a polymer, or any material, on pressurization. Although a few exceptions exist,

the phonon velocity of a material normally increases and the anharmonicity decreases, which reduces phonon scattering in crystalline materials. Thus, both these effects enhance κ . Moreover, high pressure compression reduces the thermal resistance between crystalline grains. For a semicrystalline polymer an additional feature occurs because of the different properties of the amorphous and crystalline parts. An amorphous phase is normally more compressible than a crystalline phase, which means that the volume fraction of the crystalline phase (V_c) increases with pressure [16]. As shown in Fig. 1b, only the highly crystalline UHPE shows a weakly accelerated increase of κ with pressure. Since crystalline materials typically show stronger and more linear pressure dependencies of κ than amorphous materials, it is reasonable to attribute the feature to the high crystallinity and increased fold length of UHPE. That is, highly crystalline ECC-type of UHPE shows polymer phonon-like properties similar to those of polycrystalline, low-molecular weight, materials.

The density dependence of κ is commonly described by the Bridgman parameter, or g -value, which is defined as $g = -(d \ln \kappa) / (d \ln V)$. The results for UHPE give $g = 5.3$ and 7.5 before and after treatment, respectively, which suggests a large g -value for fully crystalline UHPE with ECCs.

Fig. 2. (a). Thermal conductivity of amorphous (open symbols) and crystalline (filled symbols) UHPE as functions of pressure at 298 K, calculated from Eq. 1 (triangles) and Eq. 2 (squares), respectively. (b). Crystalline volume fraction of pristine (bottom) and treated UHPE (top) versus pressure at 298 K.

To further explore the change in κ towards a fully crystalline material we can estimate κ of the crystalline phase and the amorphous phase by assuming that PE can be modeled as a two-phase system with spherically-shaped crystalline particles dispersed as islands in a continuous amorphous phase. In this model, the thermal conductivity of PE, κ_{PE} , is expressed as [17, 18]

$$\kappa_{PE} = \kappa_a \cdot \frac{2 \cdot \kappa_a + \kappa_c + 2 \cdot V_c (\kappa_c - \kappa_a)}{2 \cdot \kappa_a + \kappa_c - V_c (\kappa_c - \kappa_a)} \quad (1)$$

where κ_a and κ_c are κ of the amorphous and crystalline phases, respectively. V_c is the volume fraction of crystallinity (Fig. 2b), which is slightly different from the (mass) fraction of crystallinity determined by DSC. The results for V_c were determined from the

volume versus pressure data of the crystalline and amorphous phases of PE [16, 19]. We thus obtained κ_a and κ_c , shown in Fig. 2a, by inserting two independent values of κ and V_c of UHPE before and after HP&HT treatment.

Using a similar two-phase assumption, but with thermally anisotropic inclusions embedded in an amorphous matrix, Choy and Young proposed a slightly different model for semicrystalline polymers: [20]

$$\frac{\kappa_{PE} - \kappa_a}{\kappa_{PE} + 2\kappa_a} \cong C \left(\frac{2}{3} \frac{\kappa_{\perp} - 1}{\kappa_{\perp} + 2} + \frac{1}{3} \right) \quad (2)$$

where $\kappa_{\perp} = \kappa_c / \kappa_a$, and $\kappa_{\perp}$ is κ perpendicular to the chain direction of a crystallite, and C is the degree of crystallinity. In general, $\kappa_{\perp}$ is close to 1, which is also the value adopted here [21]. The results for κ_a and κ_c thus calculated are shown in Fig. 2a.

The results from these calculations provide estimates for κ of polycrystalline bulk UHPE (κ_{c_UHPE}), i.e. a sample with randomly oriented ECCs, as well as for amorphous UHPE (κ_{a_UHPE}). In the first model (Eq. 1), the latter show the typical behavior for amorphous polymers with a relatively weak pressure induced increase of κ , which levels off at high pressure. The $\kappa_{a_UHPE}(1.5)/\kappa_{a_UHPE}(1 \text{ atm}) \approx 1.6$ of Eq. 1 gives a density dependence of $\kappa_{a_UHPE}(1 \text{ atm})$ of $g=2.4$, which is in the range 2-4 typically observed for g -values of amorphous polymers [22]. Eq. 2 predicts a larger value for about $g=5.3$, i.e. the same as the measured value for the semicrystalline polymer before treatment, and also a weakly accelerating pressure induced increase of κ .

These values are in sharp contrast to the estimated pressure dependence of κ of the crystalline phase. In the case of Eq. 1, $\kappa_{c_UHPE}(1.5) / \kappa_{c_UHPE}(\text{atm}) \approx 5.3$, suggesting that κ_c is strongly pressure dependent with an increase of over 400%. This gives a density dependence of $g=14$, i.e. significantly larger than that of the amorphous part (2.4). This

value is in the upper range for well-ordered crystals, e.g. close to that of crystalline glycerol ($g=13$) [23]. Eq. 2 predicts a smaller value of about 9.1. Although Eq. 1 suggests a surprisingly large g -value for fully crystalline UHPE with ECCs, it seems to produce more realistic values than those of Eq. 2. This deduction follows from the good agreement between both the pressure behavior of κ and the g -value of amorphous UHPE compared to those of other amorphous polymers. Moreover, the large increase in the pressure dependence of κ caused by the HP&HT treatment, despite that 20-30% amorphous UHPE remains, corroborates the predicted large g -value of fully crystalline UHPE with ECCs.

Fig. 3a shows κ plotted against temperature for UHPE at 0.05, 0.5 and 1.5 GPa. The increasing κ with decreasing temperature for the treated samples is typical of crystals whereas amorphous materials show a weakly decreasing κ . In the Debye model, [24] the former effect is explained mainly by an increased phonon mean free path due to diminishing phonon-phonon scattering with decreasing temperatures. The model predicts $\kappa \propto T^{-1}$ for crystals at temperatures near and above the Debye temperature. By fitting $\kappa \propto T^{-x}$, we find that the values for x of treated UHPE are, respectively, 0.71, 0.66 and 0.58 at 0.05, 0.5 and 1.5 GPa. The corresponding values for x before treatment are 0.41, 0.33, and 0.24, i.e. significantly smaller. Thus, κ of UHPE changes towards more crystalline-like behavior after treatment and comes relatively close to that of common polycrystalline materials. This is different from the results of HDPE and LDPE, for which x did not change much as a result of the treatment. In the case of HDPE, x increased from 0.31 to 0.35 at 0.05 GPa. Thus, the HP&HT treatment was most efficient in changing the behavior of UHPE.

We conclude that the significant differences between the pressure and temperature dependence of κ of treated UHPE and those of treated LDPE and HDPE must have arisen because of the HP&HT treatment. This suggests that differences in increased crystallinity and/or folding length account for the changed behavior.

Fig. 3. (a) Thermal conductivity of UHPE measured on heating before treatment at 0.05 GPa ($\square$), 0.5 GPa ($\circ$), and 1.5 GPa (Δ) and after 0.5 GPa treatment at 0.05 GPa ($\blacksquare$), 0.5 GPa ($\bullet$), and 1.5 GPa ($\blacktriangle$). (b) Thermal conductivity of crystalline ($\blacksquare$) and amorphous ($\square$) UHPE at 0.05 GPa from 150 to 400 K from Eq. 1. (c) DSC traces of (i) HDPE, (ii) HP&HT treated HDPE, (iii) UHPE and (iv) HP&HT treated UHPE. (d) WAXD spectra of UHPE before (i) and after (ii) HP&HT treatment. The inset shows the sample orientation and X-ray setup.

In a similar manner as for the pressure behavior of κ , it is possible to estimate the temperature behavior for crystalline and amorphous PE. In this case, we have used data for UHPE at 0.05 GPa, both before and after treatment, and data for V_c were taken from refs 16 and 19. Fig. 3b shows the results for κ_a and κ_c derived from Eq. 1. The results for κ_c mimic that of normal crystals and κ_a is typical for amorphous materials.

In passing, we note that the isobaric data for $\kappa(T)$ of UHPE becomes progressively more amorphous-like with increasing pressure for both the treated and untreated samples. To further investigate this, and in analogy with the Matthiessen's rule for electrical resistivity, we express the total thermal resistance (κ^{-1}) as [23]

$$\kappa^{-1} = R_{St} + R_{Ph} \cdot T \quad (3)$$

where R_{St} is a temperature independent term associated with structural disorder, R_{Ph} is a constant that describes phonon-phonon scattering and T is the temperature in K. Fits of Eq. 3, show that both R_{St} and R_{Ph} decrease with pressure, but the decrease is more significant for the latter. In the case of treated UHPE, and for a pressure increase from 0.5 to 1.5 GPa, R_{St} decreases 30% and R_{Ph} decreases 70%. This suggests that the tendency towards more amorphous like behavior at high pressure is due to an increase in the relative importance of phonon scattering against structural disorder.

Apart from the degree of crystallinity, the extent of ECC structures is important for κ of PE. The lamellae thickening due to the treatment can be evaluated from the DSC results shown in Fig. 3c. HDPE shows a complex melting behavior with two melting peaks for a sample before treatment and, at least, three peaks for the treated sample. The two main melting peaks occur at 407 and 412 K, respectively. Wunderlich and Arakawa [25] observed a similar behavior for treated HDPE and attributed the high temperature melting

peak at 412 K to ECCs (HT-phase) and the low temperature melting peak at 407 K to thinner lamellae (LT-phase). Later, Basset et al. associated the LT-phase with spherulitic morphology and the HT-phase with sheaf-like morphology [26]. By deconvolution of the melting peaks we can obtain the fractions of LT and HT melting phases in treated HDPE (Fig. 3c). We find that about 15% of the sample is in the HT-phase, i.e. the part of the sample with a melting peak at 412 K. The general shift towards higher melting temperatures after treatment suggests an increase in lamellar thickness possibly approaching that of ECCs for the thickest lamellae of the HT phase. However, it is also obvious that a significant number of thin lamellae remained in the sample, which explains the relatively moderate change towards a more crystal-like κ in treated HDPE.

In the case of UHPE, the melting peak shifted to higher temperature ($\Delta T=10$ K) and no low temperature melting peak remained, which implies a more significant and homogeneous change in the microstructure. The untreated sample should consist of lamellae of thicknesses typically found for UHPE crystallized near 1 atm, i.e. ~ 20 nm [9, 10]. This is corroborated by an estimate of the lamellar thickness (l) using an equation for the melting point (T_f) depression [27]

$$T_f = 414.2 \cdot \left(1 - \frac{0.627}{l}\right) \quad (4)$$

where T_f and l are in units of K and nm. Ignoring possible superheating in the DSC experiment, the melting point before treatment (401.7 K), gives a lamellar thickness of 21 nm. After treatment, the DSC results give $T_f=412.4$ K, or a lamellar thickness of 140 nm. This estimate corresponds well with results for similarly treated samples of UHPE, which are based on comprehensive analyses of the microstructure [28, 29]. These studies reported lamellar thicknesses of ~ 100 nm [28] and ~ 130 nm [29] for samples which

showed almost identical crystallinity, T_f and melting peak temperature (419.8 K) as our UHPE sample. Thus, we conclude that the lamellar thicknesses of the treated UHPE sample are in the 100-150 nm range.

To further assess the changes in microstructure, we have used WAXD (Fig. 3d). The WAXD analysis shows an increased crystallinity for both UHPE and HDPE, but also that the crystals adopt, or grow in, a preferred direction with respect to the applied pressure. This is indicated by the change in the relative intensity of the (110) and (200) reflections of the orthorhombic crystals ($a=7.4 \text{ \AA}$, $b=4.93 \text{ \AA}$ and $c=2.534 \text{ \AA}$). [2] The x-ray image was taken with the as-recovered UHPE sample plate oriented as shown in the inset of Fig. 3d. The increased intensity of the (200) reflection thus implies a preferred orientation of the (200) plane, which is parallel to the sample plate surface. This means that the chains, which are oriented along the c-axis direction, also must be preferentially oriented perpendicular to the direction of the applied pressure. Considering the relatively weak changes in κ of LDPE (3.5%) and HDPE (11%), which showed similar changes in the WAXD spectra due to the treatment, this degree of changed orientational order of the crystals does not strongly affect κ .

Both WAXD and DSC results show about the same crystallinity for treated HDPE and UHPE, but the DSC results also indicate that a significant part of the HDPE crystallinity is due to crystals with lamellar thicknesses far from that of ECC structures. This explains the weak changes in the temperature and pressure dependencies of κ for HDPE despite the substantial increase of crystallinity (see Supplementary material). LDPE shows the lowest degree of crystallinity, consistent with its amorphous-like κ which decreases with

decreasing temperature (see Supplementary material) in correspondence with the behavior of other low-crystallinity polymers, e.g nylon-6 [4].

Fig. 4. (a). DTA of UHPE on heating at 0.5 GPa (i) The 1st heating shows an exothermic transformation from amorphous to crystalline phase at about 530 K. The dashed line at (i) was adopted from another independent measurement. (ii) The 2nd heating shows the endothermic orthorhombic to hexagonal phase transition at ~525 K followed by an exothermic peak at 535 K. The curves are shifted for clarity. (b). Values of κ during the 2nd heating, which were measured simultaneously with the data in (a) and indicate two equilibrium endothermic processes: the endothermic orthorhombic to hexagonal phase transition at 527 K and melting at 544 K (peak temperatures).

In order to establish the high pressure transitions we have monitored these by simultaneous, in-situ, DTA and κ measurements, but the study was hampered by frequent failures of the measurements. We thus obtained only a few successful runs. As depicted in Fig. 4a, the DTA results on UHPE show two exothermic features near 530 K and 550 K on heating at 0.5 GPa (1st heating). The first feature is likely due to an amorphous to crystalline transformation. An orthorhombic to hexagonal phase transition is also

expected (Fig. 1a), but at the equilibrium phase line, it is an endothermic reaction. Thus the initial peak can be due to a complex transformation sequence, which also involves a sluggish orthorhombic to hexagonal conversion obscured by exothermic crystallization [8]. It seems reasonable that cold-crystallization and orthorhombic to hexagonal transformation occurs concomitantly, or in close vicinity, on heating. Crystallization of the melt into the hexagonal phase has been observed also in the stability range of the orthorhombic phase [30]. Thus, when the sample is heated at 0.5 GPa, the results suggest that the kinetically constrained cold-crystallization becomes possible in close vicinity of the stability range of the hexagonal phase. The second exothermic peak at 550 K indicates another amorphous to crystalline conversion, but the peak temperature seems to be above the melting temperature. It is known that UHPE of slightly lower M_w (2500000) melts at ca. 522 K at 0.5 GPa [31]. Consequently, a melting temperature of UHPE above 550 K appears unrealistic. In fact, our data for κ (Fig. 4b) indicate that this peak occurs above the melting temperature. We are therefore led to conclude that the second peak in the DTA data at about 550 K is likely anomalous and occurs as a result of the close vicinity of the maximum temperature before cooling. (Heating to higher temperatures is precluded as it may damage the equipment.)

After cooling UHPE to room temperature, it was reheated (2nd heating). As shown in Fig. 4a, the first exothermic peak vanished, and instead the DTA data show an endothermic peak followed by two exothermic peaks. The results were confirmed by repeating the experiment (1st and 2nd heating) on another UHPE sample. The endothermic peak agrees well with the orthorhombic to hexagonal equilibrium phase line. The subsequent exothermic peak is presumably due to the amorphous to crystalline

conversion and suggests that the maximum amorphous to crystalline conversion occurs near 535 K during the 2nd heating. Fig. 4b shows κ measured during the 2nd heating. (The measurements during the 1st heating repeatedly failed during the exothermic process.) The data reveal two peaks in κ , which are typical occurrences during endothermic transitions at a phase line, i.e. at an equilibrium transition [32]. The first peak in κ corresponds well with the endothermic peak in the DTA data. The latter weak peak, which occurs in between the two exothermic DTA-peaks, suggests melting at 544 K. This corroborates the deduction that the second DTA peak is not due to an exothermic transition.

4. CONCLUSIONS

In conclusion, we have established the effect of crystallinity and microstructure on the thermal conductivity of bulk samples of LDPE, HDPE and UHPE by HP&HT treatment. Transitions were monitored by DTA and measurements of κ on heating of UHPE at 0.5 GPa revealed an exothermic transition near 530 K. This is likely associated with amorphous to crystalline conversion and indicates that the temperature of maximum rate of crystallinity increase occurs near 530 K. Treatment for 4 h at 535 K and 0.5 GPa increased significantly the crystallinity of both HDPE and UHPE, but only the latter showed a substantial change in the pressure and temperature behavior of κ . DSC results indicate a homogeneous and significant change from thin lamellae toward ECC structures in UHPE, and that many thin lamellae remained in HDPE, which accounts for the difference in the behavior of κ . These results suggest that an increase of the lamellar thickness is required to significantly improve κ of PE that consists of randomly oriented lamellae.

A two-phase model, with amorphous and crystalline phases, was adopted to estimate κ of fully amorphous and crystalline UHPE, which set the limits for κ of pure bulk PE samples with randomly oriented lamellae. In a linear extrapolation of lamellar thickness versus crystallinity, the model prediction corresponds to a 100% crystalline UHPE sample with lamellar thickness of at least ~ 300 nm. The experimental results of κ for highly crystalline UHPE with ECC structures show that the pressure and temperature dependencies become crystal-like. This is not commonly observed for bulk polymers because of their complex structure with high thermal boundary resistance and randomly oriented thin lamellae. Finally, we note that the method to alter the crystallinity can be used to assess the effect of crystallinity on the ability of fillers to promote the properties of PE, and such studies are in progress.

ACKNOWLEDGMENT

We are grateful for financial support from Magn. Bergvalls foundation, Kungl. Vetenskapsakademiens fonder, the Faculty of Science and Technology, Umeå University. We thank Dr. Åke Fransson for help with the DSC system.

Supplementary material: Thermal conductivity of LDPE and HDPE measured on heating at various pressures before and after HP&HT treatment at 0.5 GPa; Melting and recrystallization temperatures, and melting enthalpies of LDPE, HDPE and UHPE. This material is available free of charge.

REFERENCES AND NOTE:

- [1] Piringer OG and Baner AL. Plastic Packaging: Interactions with Food and Pharmaceuticals, 2nd ed. Weinheim: Wiley-VCH, 2008.
- [2] Kurtz SM. UHMWPE biomaterials handbook : ultra high molecular weight polyethylene in total joint replacement and medical devices, 2nd ed. Amsterdam: Elsevier, 2009.
- [3] Vasile C and Pascu M. Practical Guide to Polyethylene. Shrewsburg: Rapra Technology Limited. , 2005.
- [4] Yu J, Tonpheng B, and Andersson O. Macromolecules 2010;43(24):10512-20.
- [5] Gruner CL, Wunderlich B, and Bopp RC. J Polym Sci, Part A-2: Polym Phys 1969;7(12):2099-113.
- [6] Prime RB and Wunderlich B. J Polym Sci, Part A-2: Polym Phys 1969;7(12):2061-72.
- [7] Wunderlich B and Davidson T. J Polym Sci, Part A-2: Polym Phys 1969;7(12):2043-50.
- [8] Bassett DC and Turner B. Nature Phys. Sci. 1972;240(103):146-8.
- [9] Cook JTE, Klein PG, Ward IM, Brain AA, Farrar DF, and Rose J. Polymer 2000;41(24):8615-23.
- [10] Zhou H and Wilkes GL. Polymer 1997;38(23):5735-47.
- [11] Krevelen DWv and Nijenhuis Kt. Properties of Polymers: Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions, 4th ed. Amsterdam: Elsevier, 2009.
- [12] Yamanaka A and Takao T. ISRN Materials Science;2011:10.
- [13] Shen S, Henry A, Tong J, Zheng R, and Chen G. Nat Nano 2010;5(4):251-5.
- [14] Mergenthaler DB, Pietralla M, Roy S, and Kilian HG. Macromolecules 1992;25(13):3500-2.
- [15] Yu J, Tonpheng B, Gröbner G, and Andersson O. Carbon 2011;49(14):4858-66.
- [16] Pastine DJ. J Appl Phys 1970;41(13):5085-7.
- [17] Eiermann K. Kolloid-Z. Z. Polym. 1965;201:3.
- [18] Andersson P and Backstrom G. J Appl Phys 1973;44(6):2601-5.
- [19] Pastine DJ. J Chem Phys 1968;49(7):3012-22.
- [20] Choy CL and Young K. Polymer 1977;18(8):769-76.
- [21] Zhou H, Zhang S, and Yang M. J Appl Polym Sci 2008;108(6):3822-7.
- [22] Andersson SP and Andersson O. J Polym Sci Part B: Polym Phys 1998;36(9):1451-63.
- [23] Ross R. G., Andersson P., Sundqvist B., and Backstrom G. Rep Prog Phys 1984;47(10):1347-402.
- [24] Berman R. Phys Rev 1949;76(2):315-6.
- [25] Wunderlich B and Arakawa T. J Polym Sci, Part A: 1964;2(8):3697-706.
- [26] Bassett DC, Khalifa BA, and Turner B. Nature Phys. Sci. 1972;239(94):106-8.
- [27] Wunderlich B and Czornyj G. Macromolecules 1977;10(5):906-13.
- [28] Simis KS, Bistolfi A, Bellare A, and Pruitt LA. Biomaterials 2006;27(9):1688-94.
- [29] Oral E, Godleski-Beckos C, Ghali BW, Lozynsky AJ, and Muratoglu OK. J Biomed Mater Res Part B Appl. Biomater 2009;90B(2):720-9.

- [30] Rastogi S and Kurelec L. J Mater Sci 2000;35(20):5121-38.
- [31] Yasuniwa M, Haraguchi K, Nakafuku C, and Hirakawa S. Polym J 1985;17(11):1209-19.
- [32] At transitions, hot-wire measurements of κ are affected by endo- and exothermic heat, which results in anomalous results superimposed on real changes in κ . An endothermic transition occurring at an equilibrium phase line gives typically an anomalous peak in κ . This occurs when the enthalpy of the transition retards the transient heating of the hot-wire probe. The effect of a sluggish exothermic, non-equilibrium, transition on κ is more difficult to anticipate. Cold-crystallization gives a real increase in κ , which may be superimposed on an anomalous decrease caused by the heat evolution.