

Comparison of the influence of Cu micro- and nano-particles on the thermal properties of polyethylene/Cu composites

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Abstract. Polyethylene (LDPE, LLDPE and HDPE) composites with different copper (micro- and nano-sized particles) contents were prepared by melt mixing and compression moulding. The melting and crystallization behaviour of the different composites was analysed using a differential scanning calorimeter (DSC), and the thermal stability in a thermogravimetric analyser (TGA). The thermal conductivities of the samples were also determined. The DSC results show that the Cu micro- and nano-particles influence the crystallization behaviour of the polyethylenes in different ways. The extent to which the copper particles influence the crystallization behaviour of the polyethylenes also depends on the respective morphologies of the different polyethylenes. The TGA results show an observable influence of both the presence of copper and the sizes of the copper particles on the thermal stabilities of the polymers. Thermal conductivities increased with increasing Cu content, but there was little difference between the thermal conductivities of the samples containing Cu micro- and nano-particles.

Keywords: *polymer composites, polyethylene/Cu, crystallization behaviour, thermal stability*

1. Introduction

This paper forms part of a comprehensive study on the use of copper micro- and nano-particles to improve thermal conductivity in phase change materials for thermal energy storage based on polyethylene/wax blends. This paper reports on the influence of Cu micro- and nano-particles on the thermal properties of polyethylene/Cu composites for three different types of polyethylene, and changes in these properties are explained in terms of morphology differences between the different polyethylenes.

The thermal properties of polyethylenes filled with copper particles were investigated by a few groups

[1–3]. One study compared composites that contained respectively micro- and nano-sized particles [3]. The authors showed that incorporation of micro- or nano-sized Cu particles into LDPE reduced the melting temperature, increased the crystallization temperature, and lowered the degree of crystallinity of the matrix of the composites. Similar effects were observed for the melting peak temperatures, melting enthalpies and crystallinities of LDPE and LLDPE filled with copper particles [1]. It was found that the degree of crystallinity of the matrix of the nanocomposites was lower than that of the microcomposites [3]. In another study two different copper particle sizes (both in the

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micron range) were used as fillers in a PP matrix [2]. This study showed an insignificant change in matrix crystallinity. The influence of graphite, another possible filler to improve the thermal conductivity of phase change materials, on the change in the degree of crystallinity of HDPE was studied by Krupa *et al.* [4]. A slight decrease in the melting temperature of the composites was observed, which suggested that the filler reduced the lamellar thickness of the crystallites. The same behaviour was observed in another study [5], where both HDPE and PS were filled with 60 wt% of graphite. Silver-coated polyamide (PA6) particles were also used as filler for HDPE [6]. In this case a slight decrease in the degree of crystallinity with an increase in silver-coated PA6 particle content was observed.

Generally, the literature focused on the thermal conductivities of metal containing polymers. However, a few papers are devoted to the thermal stability of polyethylene filled with metals [1, 3, 7]. When LDPE/Cu nano- and micro-composites were compared [3], the thermal decomposition temperatures of the nano-composites increased sharply at low Cu nano-particle contents, and reached an optimum value at 2 wt% Cu, after which it decreased with further increase in nano-Cu content. In the case of the LDPE/Cu micro-composites, the optimum thermal stability was reached only after addition of 6 wt% Cu, but higher Cu contents did not further reduce the thermal stability. A study by Luyt *et al.* [1] showed that the thermal stability of LDPE/Cu micro-composites increased, whereas the thermal stability of LLDPE/Cu micro-composites decreased, with increasing Cu content. Yang *et al.* [8] studied the thermal stability of aligned vapour grown carbon nano-fibre reinforced polyethylene samples drawn at different take-up speeds, and all these composites showed higher thermal stability than pure HDPE.

Polymers are materials with very low thermal conductivity values that roughly vary from $0.15 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for amorphous polymers to $0.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for highly crystalline polymers such as HDPE [9]. Several inorganic materials, graphite or metallic powders, are frequently used as thermally conductive fillers [10, 11]. Silver, copper and alumina particles are the most commonly used fillers due to their high inherent thermal conductivity [5, 10–12]. Krupa *et al.* [13] demonstrated that metal-coated particles can be effectively used to

improve the thermal conductivity of, for example, HDPE. The study was based on HDPE filled with silver-coated polyamide (PA). It was found that very low silver content, if deposited on the PA particles, significantly improved the thermal conductivity of the composites. Boudenne *et al.* [2] investigated the thermal conductivity of polypropylene filled with two different sizes (23 and 230 μm) of copper particles. A non-linear increase in the thermal conductivity was observed with an increase in the volume fraction of both fillers. At a given filler concentration, a higher thermal conductivity was observed in the composite filled with the smaller Cu particles. This difference was more significant at higher filler concentrations.

2. Experimental

In this work, LDPE and LLDPE were supplied in pellet form by Sasol Polymers. LDPE has an MFI of 7.0 g/10 min (ASTM D-1238), a melting point of 106°C, a molecular weight of 96 000 $\text{g}\cdot\text{mol}^{-1}$, and a density of 0.918 $\text{g}\cdot\text{cm}^{-3}$ and LLDPE has an MFI of 1.0 g/10 min (ASTM D-1238), a molecular weight of 191 600 $\text{g}\cdot\text{mol}^{-1}$, a melting point of 124°C, and a density of 0.924 $\text{g}\cdot\text{cm}^{-3}$. HDPE was supplied in pellet form by DOW Chemicals. It has an MFI of 8 g/10 min (ASTM D-1238), a molecular weight of 168 000 $\text{g}\cdot\text{mol}^{-1}$, a melting point of 130°C, and a density of 0.954 $\text{g}\cdot\text{cm}^{-3}$. Soft paraffin wax (M3 wax) was supplied in powder form by Sasol Wax. It has an average molar mass of 440 $\text{g}\cdot\text{mol}^{-1}$ and a carbon distribution between C15 and C78. Its density is 0.90 $\text{g}\cdot\text{cm}^{-3}$ and it has a melting point range around 40–60°C. Merck Chemicals in South Africa supplied the copper powder, which was used as one of the conducting fillers. It has a melting point of 1083°C and a density of 8.96 $\text{g}\cdot\text{cm}^{-3}$, and the particles sizes were less than 38 μm determined by using a laboratory test sieve with a pore sizes of 38 μm . The copper nanoparticles were supplied by Lawrence Packaging Supply Corp., Moonachie, New Jersey, USA, Lot # R402 and the particle size was 50 nm.

All the samples were prepared by mixing the components in a Brabender Plastograph 50 ml internal mixer at 160°C and a speed of 70 rpm for 15 min. After the mixing, the samples were melt pressed at 100 bar and 160°C for 15 min.

DSC analyses were done in a Perkin-Elmer Pyris-1 differential scanning calorimeter under flowing nitrogen (flow rate $20 \text{ ml}\cdot\text{min}^{-1}$). The instrument was computer controlled and calculations were done using Pyris software. It was calibrated using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. Samples (5–10 mg) were sealed in aluminium pans and heated from -40 to 160°C at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, and cooled at the same rate. For the second scan, the samples were heated and cooled under the same conditions. The peak temperatures of melting and crystallization, as well as melting and crystallization enthalpies were determined from the second scan. All DSC measurements were repeated three times for each sample. The melting and crystallization temperatures, as well as enthalpies, are reported as average values with standard deviations.

TGA analysis was carried out on a Perkin-Elmer TGA7 thermogravimetric analyser. Samples ranging between 5 and 10 mg were heated from 30 to 650°C at a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ under flowing nitrogen (flow rate $20 \text{ ml}\cdot\text{min}^{-1}$). The instrument was computer controlled and calculations were done using Pyris software.

A Shimadzu model ZU SSX-550 Superscan scanning electron microscope was used for the SEM analyses. All the samples were frozen in liquid nitrogen, then fractured by simply breaking the specimens in an appropriate size to fit in the specimen chamber, and then mounted onto the holder. The surfaces of the samples were coated with gold by an electro-deposition method to impart electrical conduction before recording the SEM micrographs. This was done to prevent the accumulation of static electric charge on the specimen during electron irradiation.

The thermal conductivity was measured using a multi-purpose apparatus ISOMET, (Applied Precision, Bratislava, Slovakia) for non-steady measurements of thermal properties. The thermal conductivity values were calculated automatically from a time dependence of the thermal flow in the material. Samples were melt-pressed into spherical (7 cm diameter) 1 mm thick sheets in a hot-melt press at 160°C for 5 min at a pressure of 100 bar. Thereafter, measurements were made at $25\pm 2^\circ\text{C}$ with a flat probe.

3. Results and discussion

The morphologies of the composites were studied by SEM analysis of the fracture surfaces of the

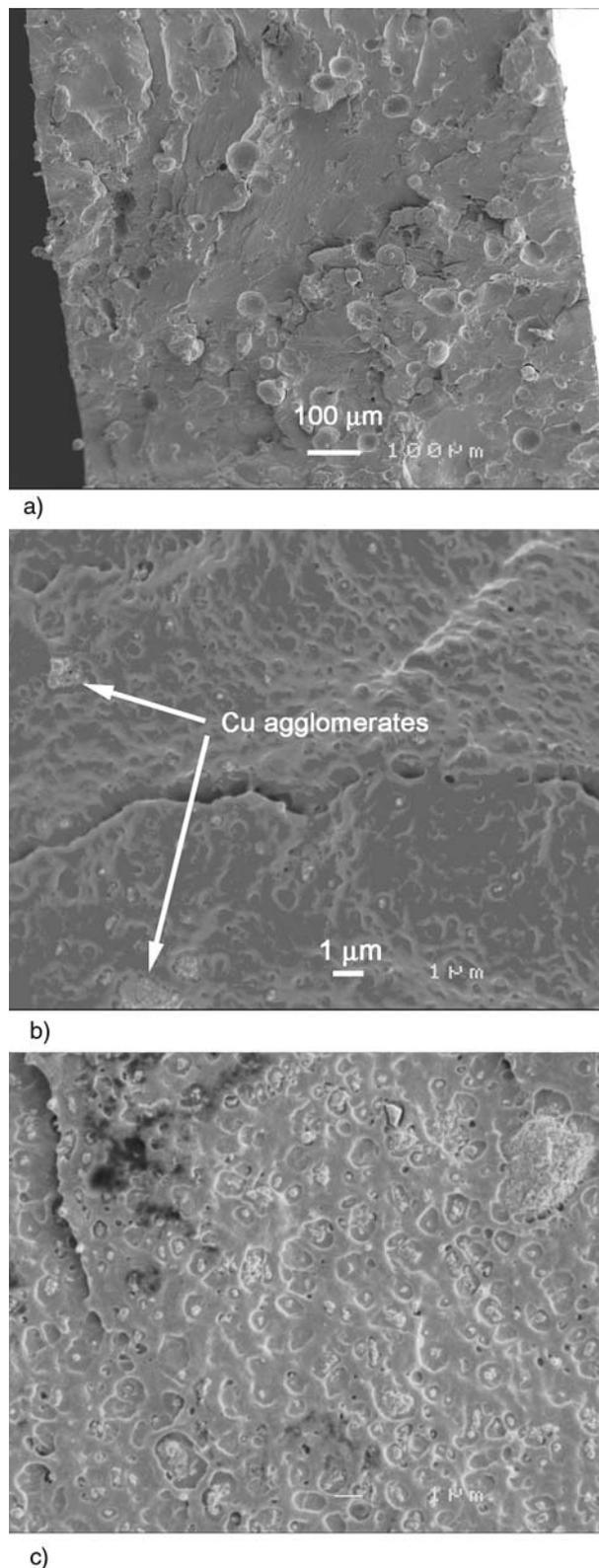


Figure 1. SEM images of (a) a 90/10 v/v LDPE/Cu micro-composite (b) a 99/1 v/v LDPE/Cu nano-composite, and (c) a 95/5 v/v LDPE/Cu nano-composite

composites. Figure 1a shows a fair dispersion of micro-particles, with no obvious agglomeration. As can be seen in Figures 1b and 1c, the Cu nano-particles are fairly well dispersed, but also form agglomerates. To optimally improve the conductivity of the composites, it is important for the particles to form a percolation network within the polymer matrices. No such network formation was observed in the SEM images of the investigated samples. In Figure 1a there seems to be voids around the Cu particles, which indicate that the interaction between the polymer and the Cu particles was weak. The lack of adhesion between the polymer and filler indicates poor interfacial interaction. As the content of Cu particles increased, the agglomeration of the particles also increased. Figure 2 shows the DSC heating curves for pure LDPE, LLDPE, and HDPE. The curves show endotherms with melting peak temperatures at 107, 128 and 135°C for LDPE, LLDPE and HDPE. Pure HDPE has a relative high enthalpy value of 149.3 J·g⁻¹, while LLDPE and LDPE have enthalpies of 86.9 and 75.4 J·g⁻¹. These values are

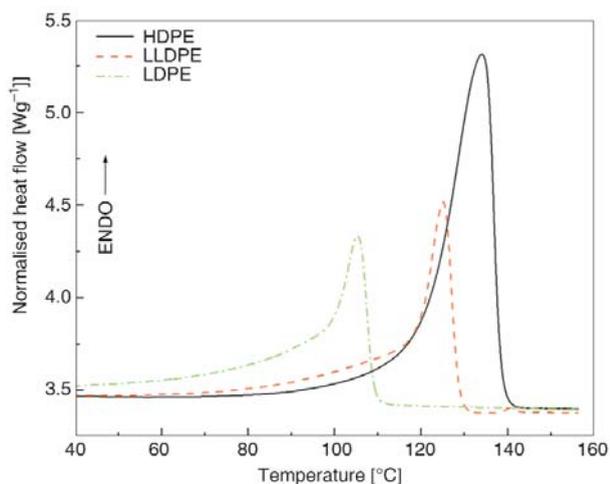


Figure 2. DSC heating curves of the pure polyethylenes

in line with the known crystallinities of the respective polyethylenes.

Table 1 shows the DSC results of the different polyethylenes and their Cu micro-composites. For the LDPE/Cu micro-composites the peak temperatures of melting did not significantly change and are within experimental error. From this it is clear that the presence of up to 20 vol% of Cu micro-par-

Table 1. DSC results for polyethylene/Cu micro-composites

v/v	$T_{p,m}$ [°C]	ΔH_m^{obs} [J·g ⁻¹]	ΔH_m^{calc} [J·g ⁻¹]	$T_{p,c}$ [°C]	ΔH_c^{obs} [J·g ⁻¹]
LDPE/Cu					
100/0	106.8 ± 1.5	75.4 ± 6.2	–	91.7 ± 0.6	-63.7 ± 7.6
99/1	107.1 ± 1.4	61.5 ± 6.3	68.8 ± 5.6	91.5 ± 1.0	-57.0 ± 6.9
97/3	106.6 ± 1.7	51.3 ± 8.3	58.1 ± 4.7	91.4 ± 0.7	-41.2 ± 4.1
95/5	106.3 ± 1.2	39.9 ± 2.6	49.8 ± 4.1	91.8 ± 1.1	-43.5 ± 4.9
90/10	106.4 ± 1.1	23.4 ± 1.8	36.2 ± 6.4	91.8 ± 0.9	-27.6 ± 3.2
85/15	105.8 ± 0.8	18.6 ± 1.6	27.8 ± 4.6	92.8 ± 0.9	-21.3 ± 3.9
80/20	106.0 ± 0.9	14.4 ± 0.4	21.9 ± 3.4	92.2 ± 0.8	-16.0 ± 3.1
75/25	105.5 ± 1.2	10.4 ± 2.7	17.9 ± 1.5	92.9 ± 1.1	-12.4 ± 2.2
LLDPE/Cu					
100/0	127.7 ± 2.1	86.9 ± 1.0	–	109.6 ± 0.9	-50.1 ± 0.8
99/1	127.9 ± 1.2	69.4 ± 4.5	79.3 ± 0.9	110.2 ± 1.0	-45.2 ± 2.0
97/3	126.8 ± 1.3	58.8 ± 4.5	66.6 ± 0.8	110.0 ± 1.3	-37.7 ± 4.1
95/5	126.2 ± 0.5	45.3 ± 9.7	57.4 ± 0.6	110.3 ± 1.3	-32.7 ± 2.5
90/10	126.5 ± 1.3	30.9 ± 7.0	41.7 ± 0.5	110.9 ± 1.7	-22.2 ± 3.4
85/15	125.4 ± 1.4	19.6 ± 4.3	31.9 ± 0.4	111.6 ± 1.2	-17.1 ± 4.5
80/20	125.5 ± 1.4	15.2 ± 3.4	25.3 ± 0.3	111.0 ± 1.3	-14.3 ± 3.1
75/25	125.4 ± 1.6	10.2 ± 2.5	20.6 ± 0.3	112.5 ± 1.3	-10.4 ± 4.2
HDPE/Cu					
100/0	134.7 ± 0.5	149.3 ± 11.7	–	113.9 ± 1.1	-134.8 ± 2.6
99/1	134.1 ± 1.3	138.1 ± 3.1	136.2 ± 10.6	114.3 ± 0.1	-132.1 ± 2.1
97/3	133.6 ± 0.1	110.4 ± 7.3	115.0 ± 9.0	115.0 ± 0.9	-110.4 ± 0.4
95/5	132.6 ± 0.3	101.8 ± 0.8	98.5 ± 7.6	114.7 ± 0.6	-97.0 ± 2.3
90/10	131.6 ± 0.2	67.4 ± 6.7	71.7 ± 5.6	115.3 ± 0.3	-72.0 ± 1.6
85/15	131.4 ± 0.2	52.3 ± 8.0	54.8 ± 4.3	115.7 ± 0.2	-53.3 ± 0.3
80/20	130.8 ± 0.5	41.4 ± 1.6	43.4 ± 3.1	116.0 ± 0.4	-43.9 ± 0.3
75/25	130.2 ± 0.2	27.2 ± 9.8	35.2 ± 2.8	116.3 ± 0.6	-34.3 ± 0.4

$T_{p,m}$, ΔH_m^{obs} , ΔH_m^{calc} , $T_{p,c}$, ΔH_c^{obs} are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, crystallization peak temperature, crystallization enthalpy

ticles in LDPE had little influence on the crystallite sizes. However, if the enthalpy values in Table 1 are compared, it is clear that the Cu micro-particles reduce the LDPE chain mobility which gives rise to a lower crystallinity. When the measured melting enthalpy values (ΔH_m^{obs}) are compared with the calculated values (ΔH_m^{calc}), it can be seen that the LDPE in the composites had significantly lower enthalpy (or crystallinity) values than would be expected if it was assumed that the Cu micro-particles had no influence on the LDPE crystallization behaviour. The ΔH_m^{calc} values were calculated from the melting enthalpy of pure LDPE and the weight fractions of LDPE in the respective composites.

A slight decrease in the melting temperature of LLDPE with an increase in Cu content is observed for the LLDPE/Cu micro-composites (Table 1). It seems as if the presence of Cu slightly reduces the LLDPE chain mobility which gives rise to smaller crystallites and a lower crystallinity. In the case of the HDPE/Cu micro-composites, a more observable decrease in the melting temperature of the composites with an increase in Cu content is observed. It seems as if the influence of Cu micro-particles on the crystallite size of polyethylene becomes more significant with decreasing branching and increasing crystallinity of the polymer. Another reason may be that the presence of highly thermally conductive Cu causes a faster heat distribution through the polymer, which will result in a lower melting temperature. Table 1 shows that the ΔH_m^{obs} and ΔH_m^{calc} values are almost the same for all the HDPE/Cu micro-composites, and therefore the presence and amount of Cu had very little influence on the HDPE crystallization behaviour.

The observations described in the previous paragraphs may be explained if it is accepted that the Cu particles will either reduce polymer chain mobility (giving rise to reduced crystallinity) or act as nucleation points for polymer crystallization (giving rise to increased crystallinity). It seems as if the chain structure (and the resultant degree of crystallinity) of the polymer determines which of the two effects will be dominant. Since LDPE and LLDPE are branched, and therefore have significantly lower crystallinities than HDPE, which confirms that the Cu particles are located in the amorphous regions of the polymers. Chain immobilization will then be the more dominant effect, and therefore these polymers show reduced crystallinity

in the presence of Cu micro-particles. Since HDPE is much more crystalline, the amorphous regions are much smaller and it is possible that crystallization will start at the Cu surfaces and that Cu particles will act as nucleation points for HDPE crystallization. This explains the slight lowering in HDPE melting temperature (indicating the presence of smaller crystallites). This is consistent with a study done by Xia *et al.* [3]. When they added 13 wt% of Cu micro-particles into an LDPE matrix, the melting peak temperatures of pure LDPE and the LDPE/Cu micro-composites were the same within experimental error. Pure LDPE had a melting enthalpy of 88 J·g⁻¹ which reduced to 76 J·g⁻¹ when 13 wt% of Cu micro-particles was introduced, and the crystallization temperature increased for the same composition. The increased crystallization temperature was explained as being due to the presence of the Cu micro-particles, which acted as nucleating agents. However, the Cu particles at the same time seemed to have immobilized the LDPE chains, giving rise to reduced crystallinity, as can be seen from the smaller melting enthalpy values.

Table 2 shows the DSC results of the different polyethylenes and their Cu nano-composites. For the LDPE/Cu nano-composites the peak temperatures of melting did not significantly change and are within experimental error. From this it is clear that the presence of up to 5 vol% of Cu nano-particles in LDPE had a negligible influence on the crystallite sizes. On the other hand, if the enthalpy values in Table 2 are compared, it is clear that the presence of the Cu nano-particles restricts the LDPE chain mobility which leads to a lower crystallinity. When the observed melting enthalpy values (ΔH_m^{obs}) are compared with the calculated values (ΔH_m^{calc}), it can be seen that the LDPE in the composites had significantly lower enthalpy (or crystallinity) values than would be expected if it was assumed that the Cu nano-particles had no influence on the LDPE crystallization behaviour.

Similarly, the copper nano-particles in the LLDPE/Cu and HDPE/Cu nano-composites had no significant influence on the melting peak temperatures of the respective polyethylenes. The observed melting enthalpies of these polyethylene composites were also lower than the calculated values. However, the differences between the observed and calculated values seem to decrease with increasing crystallinity from LDPE to LLDPE to HDPE. Since

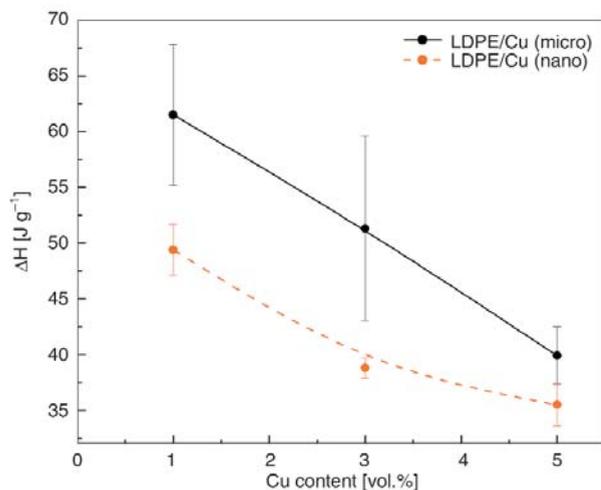
Table 2. DSC results for polyethylene/Cu nano-composites

v/v	$T_{p,m}$ [°C]	ΔH_m^{obs} [J·g ⁻¹]	ΔH_m^{calc} [J·g ⁻¹]	$T_{p,c}$ [°C]	ΔH_c^{obs} [J·g ⁻¹]
LDPE/Cu					
100/0	106.8 ± 1.5	75.4 ± 6.2	–	91.7 ± 0.6	–63.7 ± 7.6
99/1	105.9 ± 0.3	49.4 ± 2.3	68.8 ± 5.6	90.8 ± 0.1	–54.3 ± 1.9
97/3	105.7 ± 0.1	38.8 ± 0.9	58.1 ± 4.7	91.7 ± 0.3	–48.3 ± 0.8
95/5	105.3 ± 0.1	35.5 ± 1.9	49.8 ± 4.1	91.9 ± 0.1	–41.5 ± 0.6
LLDPE/Cu					
100/0	126.7 ± 2.1	86.9 ± 1.0	–	109.6 ± 0.9	–50.1 ± 0.8
99/1	126.9 ± 0.4	62.6 ± 1.4	79.3 ± 0.9	109.3 ± 0.1	–47.0 ± 4.0
97/3	125.6 ± 0.2	56.6 ± 2.3	66.6 ± 0.8	110.7 ± 0.1	–38.3 ± 2.1
95/5	126.0 ± 0.1	43.9 ± 0.7	57.4 ± 0.6	111.7 ± 0.1	–31.0 ± 2.7
HDPE/Cu					
100/0	134.7 ± 0.5	149.3 ± 9.7	–	113.9 ± 1.1	–134.8 ± 2.6
99/1	133.2 ± 0.2	132.1 ± 2.5	136.2 ± 10.6	113.8 ± 0.2	–126.2 ± 2.2
97/3	133.1 ± 0.1	106.8 ± 1.5	115.0 ± 9.0	113.9 ± 0.3	–109.5 ± 3.2
95/5	134.4 ± 1.0	82.9 ± 0.8	98.5 ± 7.6	114.7 ± 0.3	–90.0 ± 1.6

$T_{p,m}$, ΔH_m^{obs} , ΔH_m^{calc} , ΔH_c^{obs} , $T_{p,c}$, are melting peak temperature, observed melting enthalpy, calculated melting enthalpy, and crystallization peak temperature

LDPE and LLDPE are branched, and therefore have lower crystallinities than HDPE, the Cu particles are situated in the amorphous regions of these polymers. Chain immobilization will then be the more dominant effect. Since HDPE is much more crystalline, the amorphous regions are much smaller and therefore the decrease in total crystallinity is less significant.

Figure 3 shows the experimental melting enthalpies as function of Cu content for LDPE/Cu nano- and micro-composites. It can be seen that the experimental melting enthalpies of the LDPE/Cu micro-composites are higher than those of LDPE/Cu nano-composites at the same volume percentages of copper. This clearly shows that the crystallinities of the LDPE/Cu nano-composites are observably lower than those of the LDPE/Cu micro-com-

**Figure 3.** Comparison of ΔH_m^{obs} values for the melting of LDPE in LDPE/Cu micro- and nano-composites

posites, indicating that Cu nano-particles had a stronger influence on the motion and nucleation of the polymer chain segments. This behaviour indicates that the Cu nano-particles restricted the polymer chain mobility to a larger extent than the Cu micro-particles, probably because the Cu micro-particles counteract this effect through their ability to act as nucleating agents that promote the crystallization process of LDPE.

It seems as if the influence of Cu micro-particles on the crystallite size of polyethylene becomes more significant with decreasing branching and increasing crystallinity of the polymer. Tracz *et al.* [14] found that the nucleating and ordering effects of fillers on polyethylene crystallization depend to a larger extent on the nano-structure of its surface. Nano-particles do not have any nucleating effect, but they act as obstacles for the crystallization of polyethylene. Even though some nano-particle agglomerates may nucleate PE crystallization, the overall influence of the nano-particles on the crystallization of LDPE can be considered to be a retardant effect. Therefore, the degree of crystallinity of LDPE in the nano-composites is lower than that of pure LDPE. Micro-particles can nucleate PE crystallization, because they can provide sufficiently large flat domains. However, the sizes of the micro-particles are comparable to the spherulite size of LDPE, and thus the micro-particles also hinder spherulitic growth, so that the degree of crystallinity of LDPE in the presence of micro-particles is not significantly higher than that of the pure LDPE. Huang *et al.* [15] found that the addition of

2 and 4% of Al nano-particles can either facilitate or hinder the crystallization of LDPE, depending on the dispersion of the nano-particles in the polymer. The well-dispersed Al nano-particles did not have a nucleating effect and mainly acted as obstacles, but the agglomerates of Al nano-particles acted as nucleating agents and slightly improved the crystallization. The micro-particles had a nucleating effect and facilitated the crystallization process. These observations and explanations are in line with the results of our study, although in our case the presence of Cu micro-particles was found to reduce the total LDPE crystallinity, but to a smaller extent than the Cu nano-particles. In LDPE/Al micro- and nano-composites and in LDPE/TiO₂ nano-composites the melting behaviour indicated that the lamellar thickness distribution of both nano- and micro-composites did not significantly change compared to that of pure LDPE [14, 15]. The measured enthalpy values of the LLDPE/Cu and HDPE/Cu nano-composites are also lower than those of the micro-composites, but the differences are less significant (Figures 4 and 5). The reason for this is probably the higher crystallinities and lower extent of branching in these polymers, that result in a smaller influence of these particles on the polymer chain mobility. The uncertainties in the ΔH values are relatively high in the case of the microcomposites. The reason for this is probably a bigger size distribution of the micro-particles compared to the nano-particles. Unfortunately we did not statistically determine the size distribution of the micro-particles. Another interesting observa-

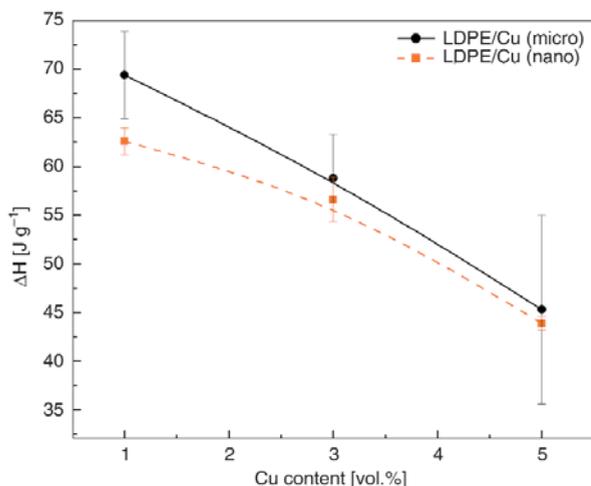


Figure 4. Comparison of ΔH^{obs} values for the melting of LLDPE in LLDPE/Cu micro- and nano-composites

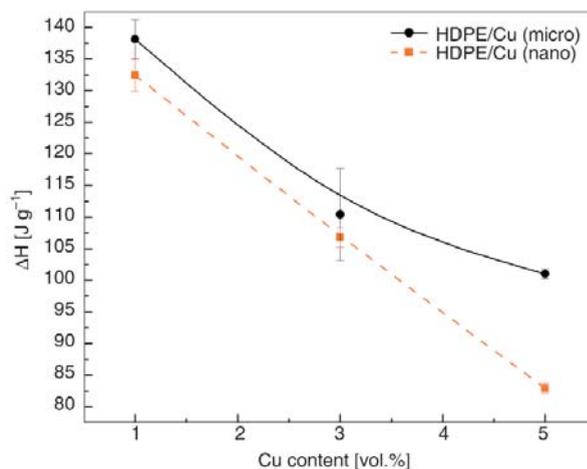


Figure 5. Comparison of ΔH^{obs} values for the melting of HDPE in HDPE/Cu micro- and nano-composites

tion is that the difference between the ΔH values of the respective micro- and nano-composites seems to decrease with increasing filler content in the case of LDPE and LLDPE, while it seems to increase in the case of HDPE. It is difficult to give an exact explanation for this observation, because a number of factors may determine the influence of inorganic particles on the crystallization behaviour of polyethylene. Amongst these are the sizes and size distributions of the filler particles, the dispersion of the particles in the polymer matrix, the effective surface areas of the particles, the crystallinities and crystallization mechanisms of the respective polymers, and the extent of interaction between the polymer and the filler particles. Depending on these factors, the filler particles will immobilize the polymer chains (reducing crystallinity) and/or act as nucleation centres (increasing crystallinity).

Although high-temperature thermal stability of these composites does not directly influence their applications, it is interesting to see how the thermal stabilities of the polymers are influenced by the presence of copper filler, and whether these observations can be explained by the same morphological features used to explain the influence of copper particles on the crystallization behaviour of the PE matrices. TGA studies were also used to establish the dispersion efficiency of the copper particles in the matrix. The TGA data of the PE/Cu micro-composites are summarized in Table 3. There is a non-linear increase in thermal stability with an increase in Cu micro-particle content up to 20 vol%. This is probably due to the inability of the polymer chains to move freely because of the presence of Cu

Table 3. Temperatures of 10% degradation and DTG peak temperatures, as well as wt% of residue, of PE/Cu micro-composites

v/v	T ₁₀ [°C]	T _{peak} [°C]	wt% residue	wt% Cu in sample
LDPE/Cu				
100/0	443.3	485.5	–	–
99/1	449.7	487.6	7.3	8.8
95/5	454.3	489.9	32.6	33.0
90/10	459.7	485.2	51.7	52.0
80/20	461.2	480.2	69.9	69.0
LLDPE/Cu				
100/0	454.1	492.9	–	–
99/1	468.5	501.8	9.7	8.9
95/5	461.4	491.7	34.0	33.1
90/10	470.4	488.9	52.0	52.2
80/20	470.4	485.4	70.3	69.5
HDPE/Cu				
100/0	467.0	500.1	–	–
99/1	463.6	496.3	8.8	8.5
95/5	469.2	497.3	32.3	33.0
90/10	455.2	485.7	50.4	51.0
80/20	458.4	471.4	69.4	69.7

micro-particles, which will retard the movement of free radical chains and inhibit the degradation process. Another reason may be that the diffusion of the volatile degradation products may be retarded by the presence of the copper particles, which will lead to these products only coming off at higher temperatures. In other studies [3, 16] it was also found that an increase in conductive filler content enhances the thermal stability of LDPE. Krump *et al.* [16] found that the thermal stability of LDPE/Cu micro-composites increased with an increase in Cu micro-particle content. Xia *et al.* [3] showed that the optimum thermal stability was reached after addition of 6 wt% Cu, but at higher Cu contents the thermal stability remained constant. Omastová *et al.* [17] showed that carbon black (CB) and modified CB in an LDPE matrix improved the thermal stability of the filled composites, with modified CB having a more significant effect.

The thermal stability of LLDPE improves with an increase in Cu micro-particles up to 1–3 vol% Cu, and the temperature at maximum decomposition rate increases for 1 vol% Cu, after which it decreases (Table 3). This is in line with the observations by Xia *et al.* [3], but differs from the observations on the LDPE/Cu composites, probably because of the higher crystallinity of LLDPE which results in more intimate contact between the Cu and

the LLDPE crystals (especially at higher Cu contents). The higher heat capacity and thermal conductivity of copper then causes more effective heat transfer to the LLDPE crystals. In the case of HDPE there is no clear trend for the influence of Cu content on its thermal stability and it seems that, within experimental error, the Cu micro-particles did not significantly influence its thermal stability. This is probably the result of a balance between thermal stability enhancement and thermal degradation initiation effects by the copper particles. The higher thermal conductivity of the metallic Cu particles may override its stiffening effect. Since HDPE is highly crystalline and inherently less thermally conductive, the transfer of heat through the entire sample is delayed. When the Cu content is above 10 vol%, there may be a strong interconnection between the Cu particles, resulting in increased thermal stability. This may also be attributed to the hindered polymer chain mobility enforced by the Cu micro-particles.

The TGA results of the PE/Cu nano-composites are summarized in Table 4. The thermal stability of LDPE and LLDPE generally increases with increasing Cu nano-particle content, but for LDPE a decrease is observed for the highest Cu content of 5 vol%. This decrease in thermal stability is probably due to the presence of Cu nano-particle agglomerates that cause an increase in energy propagation. The formation of these agglomerates was observed in the SEM results (Figure 1). The delayed thermal degradation for both LDPE/Cu and LLDPE/Cu

Table 4. Temperatures of 10% degradation and DTG peak temperatures, as well as wt% of residue, of PE/Cu nano-composites

v/v	T ₁₀ [°C]	T _{peak} [°C]	wt% residue	wt% Cu in sample
LDPE/Cu				
100/0	443.3	485.5	–	–
99/1	456.0	480.7	8.4	8.8
97/3	458.0	491.4	22.0	23.1
95/5	440.2	480.9	33.4	33.0
LLDPE/Cu				
100/0	454.1	492.9	–	–
99/1	441.8	491.7	10.5	8.9
97/3	464.6	495.9	22.5	23.0
95/5	468.1	495.6	33.4	33.1
HDPE/Cu				
100/0	467.0	500.1	–	–
99/1	409.7	460.0	9.7	8.9
97/3	437.3	484.1	26.3	23.0
95/5	460.9	486.3	31.2	33.0

nano-composites is due to the restricted chain and volatile degradation products mobility imposed by the Cu nano-particles. In all of these polyethylenes filled with Cu particles, the shift towards higher temperature is in the order of their polymer chain regularity. There is an increase in residue with increasing Cu content for all the investigated samples, and these values are in line with the initial wt% Cu mixed into the samples (Tables 3 and 4). This indicates that the presence of Cu particles did not cause any char formation.

The thermal conductivities of the PEs (LDPE, LLDPE and HDPE) filled with copper micro-particles are presented in Figure 6. A non-linear increase in thermal conductivities is observed with an increase in copper content. This is foreseeable, because the filler has a significantly higher thermal conductivity than the polymeric matrices. It can be seen that thermal conductivities of the HDPE/Cu micro-composites are higher than those of both the LLDPE/Cu and LDPE/Cu micro-composites. This is due to the higher degree of crystallinity of the HDPE matrix. In the case of semi-crystalline polymers, an increase in thermal conductivity with an increase in crystalline content was observed as a consequence of the better transport of heat in the crystalline phase [4]. The simple relation between thermal conductivity of semi-crystalline polymers and the weight fraction of the crystalline phase is expressed in terms of the additive rule [18], given by Equation (1):

$$\lambda_m = \lambda_c w_c + \lambda_a w_a \quad (1)$$

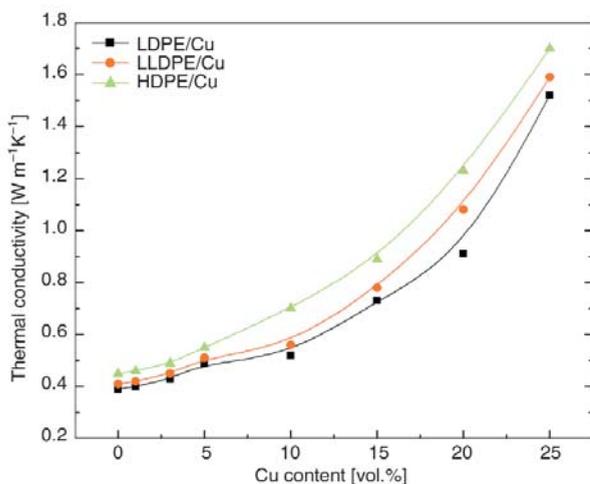


Figure 6. Thermal conductivity of the polyethylene composites as function of Cu micro-particle content

where λ_m , λ_c , λ_a are the thermal conductivities of the polymer and its crystalline and amorphous phases, respectively, and w_c , w_a are the weight fractions of the crystalline and amorphous phases of the polymer.

Generally, most inorganic fillers have much higher thermal conductivity than polymers, and therefore their incorporation into the polymers leads to an increase in thermal conductivity of the composites [5, 19]. Unfortunately, the prediction of thermal conductivity of filled polymers is very difficult and depends on the geometry and orientation of the filler particles in the matrix, the concentration of the filler, and the ratio between the thermal conductivity of the filler and the thermal conductivity of the matrix. Based on these factors, many different models have already been developed, but none of them has general validity, since most of the models are derived for regularly shaped particles, flakes or fibres that have a uniform size distribution. In this study, the copper particles were not regular.

The presence of copper nano-particles in the polymer matrices also increases the thermal conductivity of the nano-composites over that of the pure polymers (Figure 7). The copper nano-particles also improve the thermal conductivity of the composites. HDPE filled with nano-particles shows the highest thermal conductivity, similar to the micro-composites. The thermal conductivities of the nano-composites were in the same as those of the micro-composites, for the same volume fractions of copper filler.

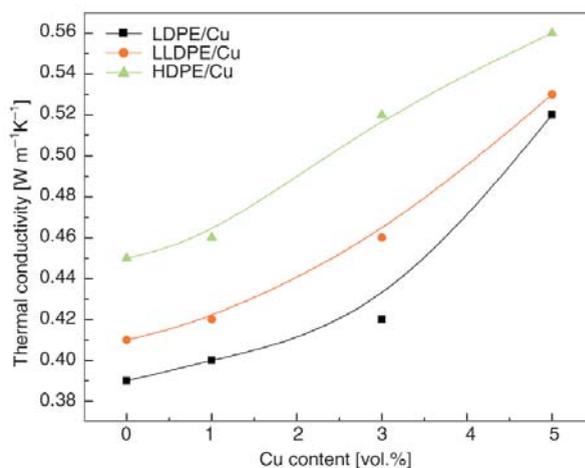


Figure 7. Thermal conductivity of the polyethylene composites as function of Cu nano-particle content

4. Conclusions

This paper discussed the morphology and thermal properties of the composites of three different polyethylenes (LDPE, LLDPE and HDPE) with Cu micro- and nano-particles. No previous paper reports such a comparative investigation. The Cu particles in the PE/Cu micro-composites were fairly well dispersed in the polymer matrix, but as the filler content increased, voids around the Cu particles were observed indicating poor interaction between the polymer and the Cu micro-particles. The lack of adhesion between the polymer and filler indicates poor interfacial interaction. The Cu nano-particles were well dispersed in the polymer matrix, except that they tended to form agglomerates. Incorporation of both Cu micro- and nano-particles into the different polyethylenes reduced the crystallinities of the different polyethylenes. Generally the nano-composites had a more significant influence because of the larger total surface area of these particles. Even though the nano-particles tended to form agglomerates, their influence was still more significant than that of the micro-particles. The micro-particles generally had a nucleating effect and facilitated the crystallization process, while the well dispersed nano-particles hindered the crystallization of polyethylene. Since linear chain polyethylenes are more difficult to decompose than the branched ones, the pure LDPE degraded at much lower temperatures compared to LLDPE and HDPE. Generally the presence of Cu particles in the polyethylenes showed an increase in thermal stability with increasing Cu content, indicating that the Cu particles either immobilized the free radical chains or inhibited the diffusion of the volatile degradation products. The Cu nano-particles had a more significant influence than the micro-particles, and the influence of both types of particles became less significant with increasing polymer crystallinity. Thermal conductivities increased with increasing Cu content, but there was little difference between the thermal conductivities of the samples containing Cu micro- and nano-particles.

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