

Comparison of the influence of copper micro- and nano-particles on the mechanical properties of polyethylene/copper composites

J. A. Molefi · A. S. Luyt · I. Krupa

Received: 16 July 2009 / Accepted: 14 September 2009 / Published online: 30 September 2009
© Springer Science+Business Media, LLC 2009

Abstract This article reports on the influence of copper content and particle size on the tensile properties of low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) mixed with up to 25 vol.% Cu micro-particles and up to 5 vol.% Cu nano-particles, and on the influence of Cu micro-particle content on the dynamic mechanical properties of these polymers. This influence depends upon the extent of branching and crystallinity in the particular polymer. The copper micro-particles seemed to have a negligible influence on the tensile strength of LDPE and HDPE, while there was quite a significant reduction in tensile strength when LLDPE was used as matrix. The elongation at break generally decreased with increasing copper content, but the effect was more significant in the case of LDPE and HDPE. The tensile modulus generally increased with increasing Cu content, but the extent of increase was lower in the case of the more crystalline HDPE. The nano-copper containing samples showed comparable properties at equivalent Cu contents. The storage and loss moduli generally increased with increasing Cu. For all three polyethylenes the β -transition (where present) was not significantly influenced by the presence and amount of copper, but the α -transition was strongly influenced, especially in the case of LDPE and LLDPE.

Introduction

Both inorganic and organic fillers play an important role in modifying the desirable properties of polymers, such as mechanical properties, thermal and electrical conductivity, permeability, and thermal stability. In conventional polymer composites, many inorganic fillers with dimensions in the micrometer range, e.g., calcium carbonate, glass beads and talc, metal, graphite, carbon black, and others were used extensively to enhance the complex behavior of polymeric composites. All these fillers give special properties to the polymers, but they significantly change the mechanical properties of the polymers. All the properties can be tailored by changing the volume fraction, shape, and size of the filler particles [1–3]. Composites are usually designed to have a set of specific properties, of which the mechanical properties are very important to both resist the mechanical stress during various practical applications and for safe manipulation.

Further improvement in the mechanical properties can be achieved by using nano-structured fillers with a larger aspect ratio such as short glass fibers, nanoclays [4–6], or fillers having a large total surface area [7]. It is logical to anticipate that the dispersion of fillers, with dimensions in the nanometer level having very large aspect ratio, stiffness and a large total surface area, in a polymer matrix could lead to even better mechanical performance.

In our previous article [8], where we discussed the thermal properties of different types of polyethylene filled with Cu micro- and nano-particles, we concluded that 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

J. A. Molefi · A. S. Luyt (✉)
Department of Chemistry, University of the Free State (Qwaqwa Campus), Private Bag X13, Phuthaditjhaba 9866, South Africa
e-mail: LuytAS@qwa.ufs.ac.za

I. Krupa
Polymer Institute, Slovak Academy of Sciences,
842 36 Bratislava, Slovak Republic

and filler indicates poor interfacial interaction. The Cu nanoparticles 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.

In this article, we compare the influence of both micro-sized and nano-sized copper particles on the mechanical and dynamic mechanical properties of three different types of polyethylene.

Experimental

In this work, low-density polyethylene (LDPE) and linear low-density polyethylene (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 g mol⁻¹, and a density of 0.918 g cm⁻³ and LLDPE has an MFI of 1.0 g/10 min (ASTM D-1238), a molecular weight of 191,600 g mol⁻¹, a melting point of 124 °C, and a density of 0.924 g cm⁻³. High-density polyethylene (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 g mol⁻¹, a melting point of 130 °C, and a density of 0.954 g cm⁻³. Merck Chemicals in South Africa supplied the copper powder, which was used as one of the conducting fillers. It has a melting point of 1,083 °C and a density of 8.96 g cm⁻³, and the particle sizes were less than 38 µm determined by using a laboratory test sieve with a pore sizes of 38 µm. The copper nano-particles 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.

A Hounsfield H5KS universal testing machine was used for the tensile analysis of the samples. The dumbbell samples were stretched at a speed of 50 mm min⁻¹ under a cell load of 250.0 N. The dumbbell samples had a total length of 75 mm, a gauge length of 24 mm, a neck width of 5 mm, and a thickness of 1 mm. About nine test samples were cut using a dumbbell cutter and they were all tested.

Stress–strain curves that indicated sample deficiencies were ignored during the final calculations of the tensile properties.

The dynamic mechanical properties of the composites were investigated using a Perkin Elmer Diamond DMA. The settings for the analyses were as follows:

Frequency 1 Hz
 Amplitude 20 µm
 Temperature range –140 to –80 °C
 Heating rate 5 °C min⁻¹
 Preloading force 0.02 N
 Length 20 mm
 Width 12.0–12.5 mm
 Thickness 1.0–1.3 mm.

Results and discussion

The tensile properties of the different PEs and their Cu micro-composites are listed in Table 1. The stress at break of all three PEs decreased with increasing Cu content. The highest decrease was observed for LLDPE, where the suppression of cold flow and orientation hardening was the most pronounced. The smallest decrease was observed for LDPE, where no orientation hardening was observed, even for the pure polymer. In all the cases no reinforcing effect of the filler was observed. This is due to a weak interfacial adhesion between the filler and the matrix as was shown by the SEM results [8].

Pure LLDPE had the highest value of stress at break. At 10 vol.% of Cu micro-particle content, the initial stress at break of LLDPE (26 MPa) decreased to a value of 14 MPa, and for LDPE it decreased from 10 to 9 MPa, while that of HDPE decreased from 16 to 10 MPa. As pointed out above, LLDPE has a very significant orientational hardening, which will always be reduced by the presence of filler particles, and therefore the decrease in stress at break was more pronounced for the LLDPE than for the LDPE or HDPE matrices. The presence of defects in front of the neck has a critical influence on the drawability. A higher concentration of the defects, caused by a higher local concentration of the filler, resulted in a steeper decrease in stress at break for the HDPE matrix, which is probably due to its higher crystalline content. Since the filler is located only in the amorphous phase, the concentration of the filler related to the amorphous content is higher in LLDPE and HDPE than in LDPE. The consequence of this is that the amorphous part in the more crystalline polymer (HDPE) is more reinforced compared to the relatively low crystalline polymer (LDPE), due to a higher local concentration of the filler in the amorphous phase. The mechanical properties of metal filled polymers are strongly affected by factors such

Table 1 Tensile properties of PE/Cu micro-composites

v/v	$\sigma_b \pm S\sigma_b$ (MPa)	$\varepsilon_b \pm S\varepsilon_b$ (%)	$E \pm sE$ (MPa)
LDPE/Cu			
100/0	10.1 \pm 0.5	336 \pm 1	120 \pm 8
99/1	9.6 \pm 0.4	325 \pm 10	135 \pm 5
97/3	9.1 \pm 0.2	223 \pm 5	155 \pm 7
95/5	8.6 \pm 0.5	86.3 \pm 10.0	158 \pm 5
90/10	8.6 \pm 1.0	19.2 \pm 1.3	191 \pm 4
85/15	8.6 \pm 0.6	20.0 \pm 3.2	192 \pm 7
80/20	9.3 \pm 0.8	19.9 \pm 5.1	207 \pm 5
75/25	9.4 \pm 0.5	10.6 \pm 6.4	219 \pm 4
LLDPE/Cu			
100/0	25.7 \pm 1.4	1054 \pm 3	123 \pm 1
99/1	20.9 \pm 1.2	911 \pm 8	171 \pm 16
97/3	19.6 \pm 1.2	874 \pm 4	169 \pm 15
95/5	18.2 \pm 0.4	857 \pm 2	141 \pm 4
90/10	14.0 \pm 0.4	741 \pm 2	194 \pm 9
85/15	12.0 \pm 0.5	669 \pm 6	176 \pm 19
80/20	8.7 \pm 0.7	454 \pm 15	222 \pm 27
75/25	8.1 \pm 1.0	278 \pm 13	237 \pm 34
HDPE/Cu			
100/0	15.6 \pm 5.3	792 \pm 3	566 \pm 8
99/1	11.7 \pm 5.8	769 \pm 4	594 \pm 3
97/3	9.1 \pm 2.2	276 \pm 5	597 \pm 2
95/5	7.1 \pm 5.4	158 \pm 2	594 \pm 3
90/10	9.5 \pm 3.4	31.5 \pm 2.5	670 \pm 4
85/15	14.6 \pm 1.3	14.5 \pm 1.8	670 \pm 4
80/20	13.2 \pm 2.8	12.8 \pm 1.5	780 \pm 7
75/25	13.8 \pm 8.7	13.8 \pm 0.7	552 \pm 3

σ_b is the stress at break and $S\sigma_b$ is the standard deviation, ε_b is the elongation at break and $S\varepsilon_b$ is the standard deviation, E is Young's modulus and sE is the standard deviation

as type, concentration, size, shape, and orientation of the filler particles [9–14]. These parameters are affected by the strength of the adhesive bond between the two phases, the type of dispersion and the amount of particle agglomeration. The influence of these factors on the tensile behavior is often difficult to separate and evaluate in a quantitative manner. Since there is no good general theory about the stress–strain behavior of metal filled polymers [9, 10], it is known from observations that the tensile strength of a material decreases with an increase in filler content [9–16]. However, it is not always the case that the stress at break decreases with an increase in filler content. For example, in the case of the HDPE composites investigated in this article, the initial decrease is caused by a reduction in the drawability as well as by the presence of defects. However, if there is good interaction between the polymer and the filler or reinforcement due to immobilization of the polymer chains onto the filler surface, there may be a

reinforcing effect and an increase in stress at break is observed [9]. This can result in stress at break values that are higher than that of the pure polymer.

The elongation at break data of the PE/Cu micro-composites are summarized in Table 1. There is a significant drop in the drawability after addition of the copper particles. A decrease in the elongation at break for polymers filled with inorganic fillers is always observed [9–14], and the presence of defects in front of the neck has a critical influence on the drawability. According to Rusu et al. [14] the occurrence of particle agglomeration is responsible for the appearance of metal particle contacts, instead of polymer–metal particle contacts, characterized by a total lack of adhesion. In our case a considerable decrease in the elongation at break of the PE/Cu micro-composites were observed with an increase in Cu content.

It can be seen in Table 1 that the elongation at break of pure LLDPE and HDPE show higher values than pure LDPE, because when force is applied, the polymer chains have enough space and time to orientate, which is the result of the chemical structure of crystalline polymers. Immediately when the chains are oriented, they start to form orientation crystallinity, which evokes an increase in the strength of a sample. Adding filler to the polymer matrix reduces chain mobility, giving rise to a rapidly decreasing elongation at break. When 10 vol.% of copper micro-particles were incorporated into the respective matrices, the initial elongation at break of pure LLDPE decreased from 1,054 to 740%, for pure HDPE it decreased from 791 to 32%, and for pure LDPE it decreases from 336 to 19%.

The Young's modulus data of the pure the PEs and their Cu micro-composites are summarized in Table 1. Young's modulus slightly increased with an increase in copper content for all three polyethylenes, except for HDPE at the highest filler content. The size and distribution of the filler plays a significant role, since the filler is much stiffer than the polymer matrix, and the stiffness increases with increasing filler content. The extent depends on the filler surface area. This is common behavior for polymers filled with inorganic fillers [10–12, 14]. The modulus of the HDPE composites increased up to 20 vol.% of copper, but for the 25 vol.% Cu containing composite the value dropped even lower than that of pure HDPE. This is probably caused by insufficient de-wetting of the filler and de-bonding of the matrix, similar to the case of stress at break, since the bonds between the polymer and the Cu particles are weak. Similar behavior was observed where HDPE was filled with an inorganic filler [13].

The stress at break results for the PE/Cu nano-composites are presented in Table 2. The presence of copper nano-particles in the PE matrices slightly decreased the stress at break of the nano-composites. The lower stress at break values of the nano-composites could be due to a

Table 2 Tensile properties of the PE/Cu nano-composites

v/v	$\sigma_b \pm S\sigma_b$ (MPa)	$\varepsilon_b \pm S\varepsilon_b$ (%)	$E \pm sE$ (MPa)
LDPE/Cu			
100/0	10.1 ± 0.5	336 ± 1	120 ± 8
99/1	8.6 ± 0.4	153 ± 1	134 ± 4
97/3	8.9 ± 0.2	55.8 ± 1.2	158 ± 4
95/5	7.4 ± 0.5	14.4 ± 4.0	159 ± 7
LLDPE/Cu			
100/0	25.7 ± 1.4	1054 ± 3	123 ± 1
99/1	22.3 ± 1.1	917 ± 4	216 ± 8
97/3	23.6 ± 0.6	900 ± 3	260 ± 6
95/5	18.7 ± 1.4	749 ± 5	273 ± 4
HDPE/Cu			
100/0	15.6 ± 5.3	792 ± 3	566 ± 8
99/1	10.3 ± 2.2	402 ± 4	621 ± 6
97/3	8.6 ± 4.1	33.9 ± 7.7	709 ± 7
95/5	7.8 ± 6.3	19.3 ± 7.5	726 ± 5

σ_b is stress at break and $S\sigma_b$ is the standard deviation, ε_b is elongation at break, $S\varepsilon_b$ is the standard deviation, E is Young's modulus and sE is the standard deviation

number of reasons such as weak interfacial bonding between the Cu nano-particles and matrix interfaces, aggregates of Cu nano-particles and nano-size processing related defects. There were no obvious differences in stress at break values between the HDPE micro- and nano-composites. The values for the nano-composites were slightly lower for LDPE and slightly higher for LLDPE than those of the micro-composites. It is difficult to establish a relationship between these observations and the respective morphologies of the polyethylenes.

The dependence of elongation at break on Cu nano-particle content is summarized in Table 2. There was a decrease in elongation at break with an increase in Cu nano-particle content for all the investigated nano-composites. The decrease is much more significant for HDPE and LDPE than it is for LLDPE. The decrease is also more significant for the nano-composite samples compared to the micro-composite samples. The reason for the difference in behavior between LLDPE on the one hand and LDPE and HDPE on the other hand is not obvious. However, the more significant decrease for the nano-composites compared to the micro-composites may be explained in terms of the increase in number of nano-particles in the polymer matrix and the accompanying increase in number of defect points.

Young's modulus of the nano-composites as function of the Cu nano-particle content is summarized in Table 2. The values increase with an increase in filler content for all three polymers. If the increase is taken as a percentage of the modulus value of the pure polymer, the increase is much more pronounced for LLDPE, followed by HDPE,

while the LDPE moduli did not change appreciably with increasing Cu content. The modulus of the LDPE micro-composites are almost the same as those of the nano-composites, while those of the LLDPE and HDPE micro-composites are lower than those of the nano-composites. All these observations may be explained in terms of the fact that the Cu particles are most probably located in the amorphous regions of the respective polymers. The higher the amorphous content, the weaker the influence of the Cu particles on the overall chain mobility of the polymer. As a result of their higher total surface area, the nano-particles have a stronger influence, especially in the more crystalline polyethylenes.

The DMA storage modulus results of the PE/Cu micro-composites are shown in Figs. 1, 2, and 3. Generally, for all three polyethylenes, the storage modulus increased with an increase in Cu content. This increase is attributed to the

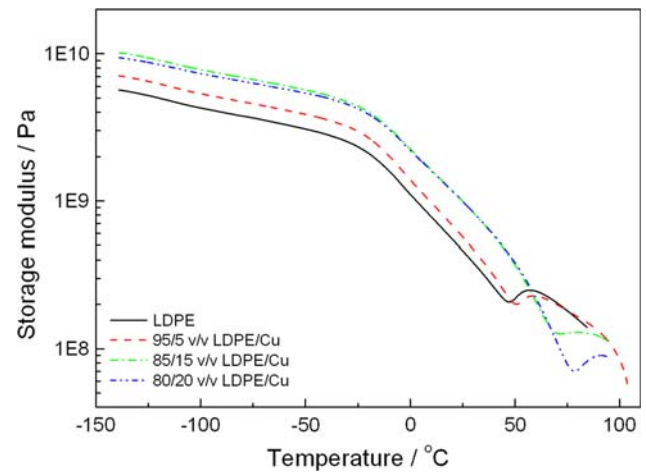


Fig. 1 DMA storage modulus curves of pure LDPE and LDPE/Cu micro-composites

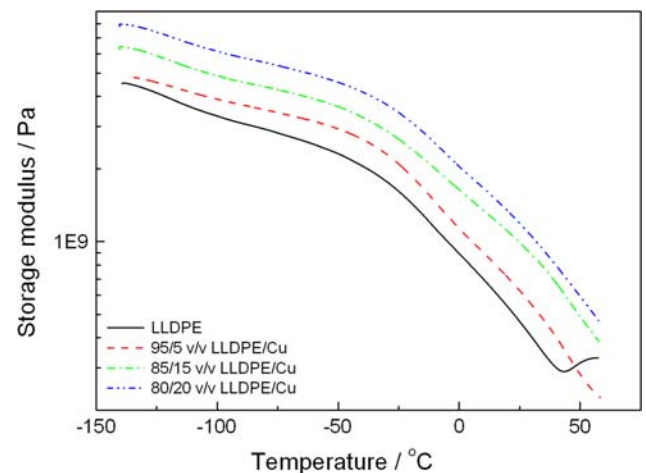


Fig. 2 DMA storage modulus curves of pure LLDPE and LLDPE/Cu micro-composites

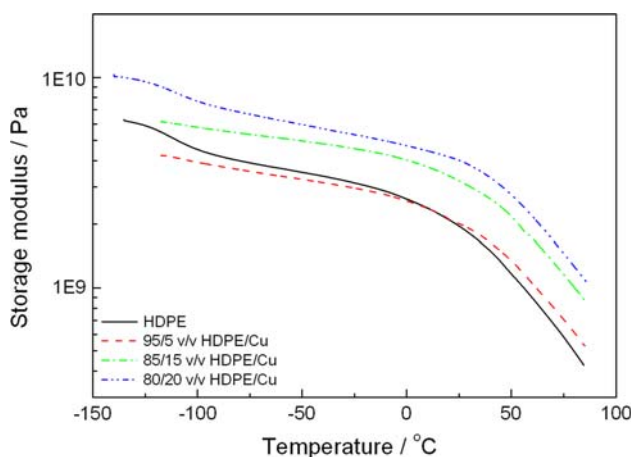


Fig. 3 DMA storage modulus curves of pure HDPE and HDPE/Cu micro-composites

presence of Cu particles which resulted in the stiffening of the polyethylene matrices. This is in line with the tensile results, where Young's modulus increased with increasing Cu particle contents. The storage moduli for all the samples decreased with increasing temperature, and the slopes of the lines change at the transition temperatures, that are different for the different types of polyethylene. These relaxations are due to an increased mobility in the polyethylene chains. However, for LDPE and its Cu-composites and for pure LLDPE the storage modulus curves show a peak around or above 50 °C. This is not a typical observation for the storage modulus as function of temperature, and currently the only explanation is that it is related to the melting of the thinnest lamellae.

The loss modulus curves for the different polyethylenes and their Cu micro-composites are presented in Figs. 4, 5, and 6. Three loss maxima are found at about -121 (γ -transition), -16 (β -transition), and 66 °C (α -transition)

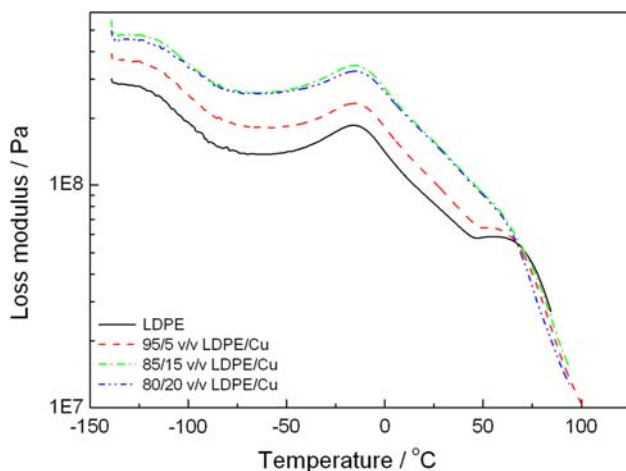


Fig. 4 DMA loss modulus curves of pure LDPE and LDPE/Cu micro-composites

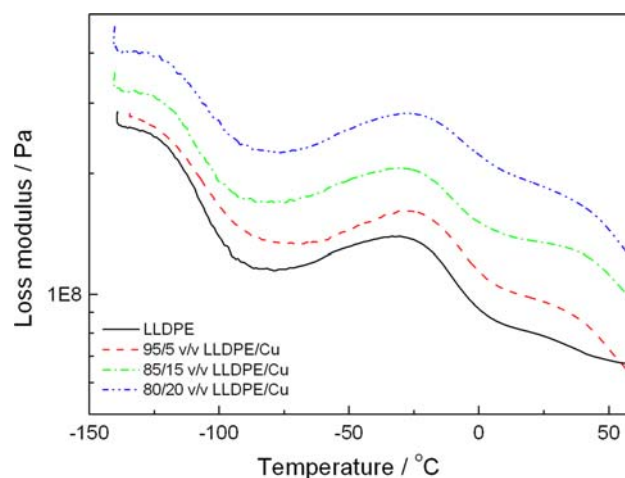


Fig. 5 DMA loss modulus curves of pure LLDPE and LLDPE/Cu micro-composites

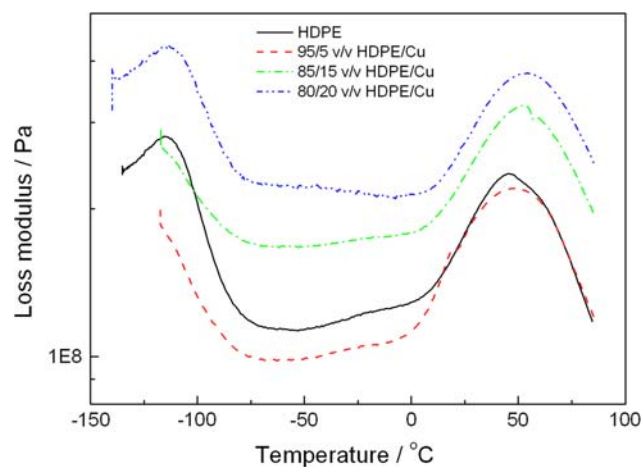


Fig. 6 DMA loss modulus curves of pure HDPE and HDPE/Cu micro-composites

for LDPE, and at about -125 , -27 , and 25 °C for LLDPE. For HDPE two loss maxima are found at about -112 (γ -transition) and 48 °C (α -transition). For the purpose of this study, the β -transitions at -16 °C for LDPE and -27 °C for LLDPE can be seen as their glass transition temperatures. The glass transition is where the chains in the amorphous regions start with coordinated large-scale motion, and it is therefore not observable in the highly crystalline HDPE. The glass transition in highly crystalline polymers (HDPE) is difficult to identify [17], and this is in line with the current observations. Although there is a controversy concerning the glass transition of polyethylenes [17], it is generally agreed that the β -transition is associated with the transition of branch points. For LDPE, which is a branched polymer, a clear β -transition peak was also detected by other researchers [18]. Sirotkin and

Brooks [19] reported that for HDPE the β -transition is usually absent. This relaxation is, therefore, generally attributed to segmental motions in the non-crystalline phase. The α -transition is observed between 20 and 70 °C and is attributed to chain movements in the crystalline region. The position and intensity of this transition depends on many factors like the heating rate, density, and branching [20]. An increase in density (which normally is the result of increased crystallinity) increases the intensity of this peak, and therefore the α -transition is more prominent in the case of HDPE. An increase in the loss modulus with an increase in copper particle content was observed for most of the samples. The higher loss modulus implies lower elastic recovering, which can be attributed to the higher polymer rigidity.

The damping factor, $\tan \delta$, is the ratio of the loss modulus to the storage modulus and gives information on the relative contributions of the viscous and elastic components of viscoelastic materials. Figures 7, 8, and 9 present the $\tan \delta$ curves of the pure polyethylenes and their Cu-composites. In addition to the γ - and β -transitions, pure LDPE shows two transitions that may be called the α - and α^* -transitions. The α -transition is related to larger chain segments in the amorphous phase that start to move, while the α^* -transition is associated with the slippage between crystallites [20]. As the Cu particle content increases, the composites show only one transition in this temperature region, indicating that the Cu particles suppress large-scale chain movement in LDPE through chain immobilization. As a result the α - and α^* -transitions merge into a single, more intense transition during which both large-scale chain movement and slippage of crystallites occur. Another explanation for the double transition around 50 °C may be that there is melting of the smallest crystallites closely followed by interlamellar shear of the larger crystallites.

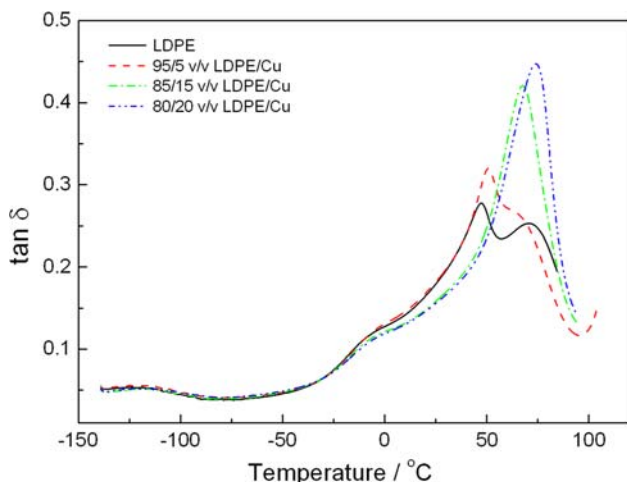


Fig. 7 DMA damping factor curves of pure LDPE and LDPE/Cu micro-composites

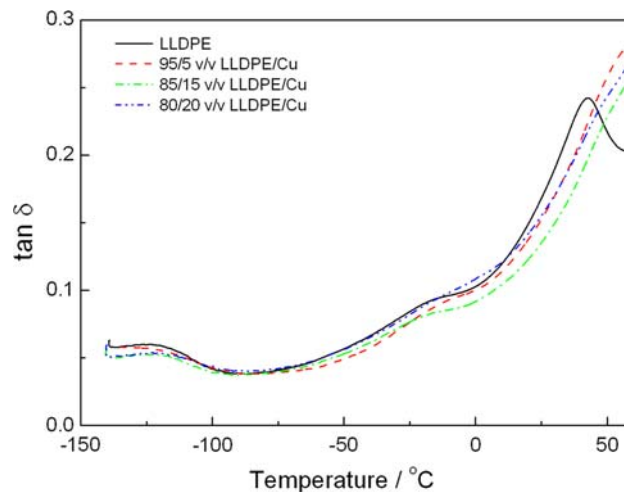


Fig. 8 DMA damping factor curves of pure LLDPE and LLDPE/Cu micro-composites

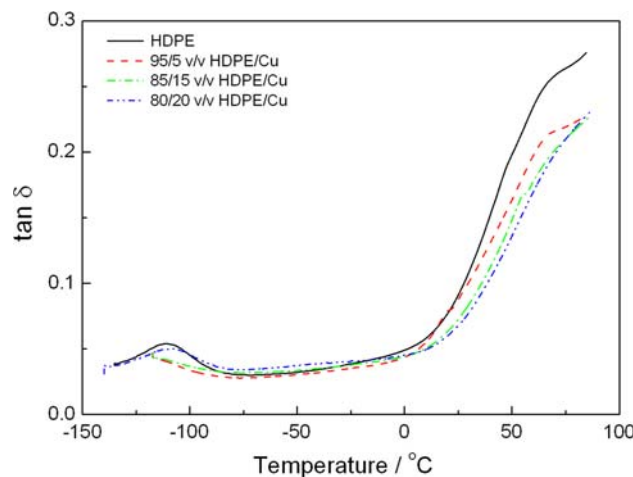


Fig. 9 DMA damping factor curves of pure HDPE and HDPE/Cu micro-composites

The presence of Cu-particles seems to inhibit the melting process (see storage modulus curves in Fig. 1), so that both processes occur in the temperature range of the α -transition.

The damping factor curves of LLDPE and its composites show γ -, β -, and α -transitions. In this case there is, however, only one peak in the high temperature region. This is probably due to the higher crystallinity of LLDPE, as well as the absence of premature melting. The α -transition also appears at a higher temperature for the composites compared to the pure polymer, which is the result of the immobilization of the polymer chains in the presence of the Cu particles. In the highly crystalline HDPE and its Cu micro-composites there is no β -transition, while the strong α -transition is the result of interlamellar shear. Since the Cu particles are probably located in the small

amorphous areas between the crystallites, they should have an influence on the slippage between crystallites. This is, however, not clear from the presented curves in Fig. 9.

Conclusions

The influence of the presence of copper particles in different polyethylene matrices depends upon the extent of branching and crystallinity in the particular polymer. In this investigation copper micro-particles seemed to have a negligible influence on the tensile strength of LDPE and HDPE at copper contents up to 25 vol.%, while there was quite a significant reduction in tensile strength when LLDPE was used as matrix. The elongation at break generally decreased with increasing copper content, but the effect was more significant in the case of LDPE and HDPE. The tensile modulus generally increased with increasing Cu content, but the extent of increase was lower in the case of the more crystalline HDPE. The nano-copper containing samples showed comparable properties at equivalent Cu contents. The storage and loss modulus generally increased with increasing Cu content over the whole investigated temperature range for all three polyethylenes. For all three polyethylenes the β -transition (where present) was not significantly influenced by the presence and amount of copper, but the α -transition was strongly influenced, especially in the case of LDPE and LLDPE.

Acknowledgements The National Research Foundation of South Africa (GUN 62693), the University of the Free State and, in part, the Scientific Grant Agency of the Ministry of Education of Slovak

Republic and the Slovak Academy of Sciences (Project No. 2/0063/09) are acknowledged for financial support of this research.

References

1. Long Y, Shanks RA (1996) *J Appl Polym Sci* 61:1877
2. Bartczak Z, Argon AS, Cohen RE, Weinberg M (1999) *Polymer* 40:2347
3. Misra RKD, Nerikar P, Bertrand K, Murphy D (2004) *Mater Sci Eng A* 384:284
4. Unal H, Mimaroglu A, Alkan M (2004) *Polym Int* 53:56
5. Takahara A, Magome T, Kajiyama T (1994) *J Polym Sci Part B: Polym Phys* 32:839
6. Dibenedetto AT (2001) *Mater Sci Eng A* 302:74
7. Lebaron PC, Wang Z, Pinnavaia TJ (1999) *Appl Clay Sci* 15(1–2): 11
8. Molefi JA, Luyt AS, Krupa I (2009) *eXPRESS Polym Lett* 3(10):639
9. Krupa I, Novák I, Chodák I (2004) *Synth Met* 145:245
10. Gungor A (2006) *J Appl Polym Sci* 99:2438
11. Krupa I, Chodák I (2001) *Eur Polym J* 37:2159
12. Krupa I, Miková G, Novák I, Janigová I, Nógellová Z, Lednický F, Prokeš J (2007) *Eur Polym J* 43:2401
13. Luyt AS, Molefi JA, Krump H (2006) *Polym Degrad Stabil* 91:1629
14. Rusu M, Sofian N, Rusu D (2001) *Polym Test* 20:409
15. Nurazreena, Hussain LB, Ismail H, Mariatti M (2006) *J Thermoplast Comp Mater* 19(4):413
16. Tan S, Zhang M, Rong M, Zeng H (2004) *Polym Comp* 20(3):406
17. Turi EA (1997) *Thermal characterization of polymer materials*, 2nd edn. Academic Press, New York
18. Ward IM (1971) *Mechanical properties of solid polymers*, 2nd edn. Wiley, New York
19. Sirotkin RO, Brooks NW (2001) *Polymer* 42:9801
20. Menard KP (1999) *Dynamic mechanical analysis: a practical introduction*. CRC Press, Boca Raton, USA