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Micro-mechanisms of deformation in polyethylene/clay micro- and nanocomposites

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ABSTRACT

Incorporation of clay in polymers is known to improve mechanical properties such as tensile modulus and tensile strength, but to generally decrease elongation at break and toughness. However, recent studies reported an increase in elongation at break for linear low density polyethylene based nanocomposites. In this work, the tensile properties of clay micro- and nanocomposites based on high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) of similar molecular weights were evaluated. LLDPE micro- and nanocomposites exhibited an extraordinary enhancement in toughness compared to LDPE or HDPE microcomposites. Based on electron microscopy and on acoustic emission and volume strain measurements during tensile testing, micro-mechanisms of deformation in polyethylene/clay micro- and nanocomposites were proposed.

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1. Introduction

Layered silicate based polymer nanocomposites have attracted considerable interest since nanometric scale dispersion was obtained in polyamide/clay composites [1]. Compared to conventional micro-fillers, layered silicates are expected to lead to remarkable properties when delaminated in polymeric matrices, resulting in material valorization at moderate cost [2]. Montmorillonite, a natural clay having aspect ratio higher than 100, is frequently used as reinforcement for polymer nanocomposites. Compared to the pure polymer matrix, polymer/montmorillonite composites exhibit significant increases in mechanical properties such as tensile modulus and tensile strength. This effect is even more pronounced when the clay forms an exfoliated rather than a micro-dispersed structure. However, it has generally been observed that the incorporation of montmorillonite in polymers results in a reduction of the elongation at break. To our knowledge, only few studies have reported an increase in the elongation at break [3–5]. Xu et al. [5] reported an increase of 30% in elongation at break for glassy poly(lactide-co-glycolide)/clay (3 wt.%) nanocomposites. Microscopic studies revealed that the presence of clay modified the micro-mechanisms of deformation compared to the pure matrix, favoring multiple crazing and shear yielding. In the field of polyethylene/clay composites, most studies reported a decrease in elongation at break [6–15], at the exception of two studies involving LLDPE matrices [16,17]. Zhang and Sundararaj [16] observed an increase of 50% in elongation at break for LLDPE/

LLDPE-g-MA/clay (5 wt.%) nanocomposites. They attributed this particular behavior to the formation of an exfoliated structure and to a strong adhesion at the polymer/clay interface provided by the addition of the maleated LLDPE-g-MA coupling agent. However, Stoeffler et al. [17] reported an increase in elongation at break of more than 100% for both LLDPE/clay (4–6 wt.%) microcomposites and LLDPE/LLDPE-g-MA/clay (4–6 wt.%) nanocomposites. This result suggests that the introduction of a maleated coupling agent is not the only factor responsible for toughness enhancement in those composites.

In this work, the structural and mechanical properties of polymer/clay micro- and nanocomposites based on HDPE, LDPE and LLDPE having similar molecular weights were evaluated. In order to understand the effect of the clay on the micro-mechanisms of deformation, acoustic emission and volume strain measurements were performed upon tensile testing. Both techniques have proved to provide interesting information about the mechanisms of deformation in pure polymers [18], conventional composites [19,20] and polymer/clay micro- and nanocomposites [21,22]. Results were coupled to a detailed analysis of the micro- and nanostructure by SEM and TEM.

2. Materials

Five grades of polyethylene (HDPE, LDPE, LLDPE) with a melt flow index of ~1 g/10 min (190 °C/2.16 kg) were kindly provided by Nova Chemicals. In addition, two LLDPE-g-MA coupling agents were obtained from Arkema and Polyram. The characteristics of polyethylene matrices and coupling agents are presented in Table 1.

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Table 1

Properties of the polyethylene matrices and coupling agents.

Resin	Type	MFI – 190 °C/2.16 kg (g/10 min)	ρ (g/cm ³)	T_c (°C)	T_m (°C)	M_w (g/mol)	M_w/M_n	Additives ^c
HDPE (Sclair 19G)	HDPE	1.2 ^a	0.960 ^a	118 ^b	133 ^b	101,760 ^a	5.29 ^a	PS
LDPE (Novapol LFY819A)	LDPE	0.75 ^a	0.919 ^a	98 ^b	109 ^b	91,576 ^a	4.48 ^a	PS
LLDPE-4 Novapol PF118F)	LLDPE (ethylene/butene)	1.0 ^a	0.918 ^a	111 ^b	124 ^b	99,200 ^a	3.09 ^a	PS
LLDPE-6 (Novapol TF119F)	LLDPE (ethylene/hexene)	1.0 ^a	0.918 ^a	107 ^b	123 ^b	110,200 ^a	3.17 ^a	PS
LLDPE-8 (Sclair FP120A)	LLDPE (ethylene/octene)	1.0 ^a	0.920 ^a	107 ^b	120 ^b	103,300 ^a	3.33 ^a	PS
C ₁ (Orevac 18302 N)	LLDPE-g-MA (MA = 0.2–2.0 wt.%)	1.4 ^a	0.912 ^a	114 ^b	124 ^b	125,000 ^d	Unknown	Unknown
C ₂ (Bondyram 4001)	LLDPE-g-MA (MA = 1.03 wt.%)	4.0 ^a	0.930 ^a	111 ^c	123 ^c	69,000 ^d	Unknown	Unknown

^a Data from supplier.^b Determined using a TA Instruments DSC Q1000 (10 °C/min).^c PS: process stabilizer.^d Estimated according to the following equation: $\eta_0 = K \cdot M_w^{3.4}$. The values of plateau viscosity were determined by oscillatory rheometry at 200 °C for all polymers. The value of K was calculated using the data of Nova Sclair FP120A. It should be noted that those values are indicative only, since the previous equation is strictly valid for linear polymers having the same chemical structure.

The clay, dimethyl dihydrogenated tallow ammonium modified montmorillonite (Cloisite 20A), was purchased from Southern Clay Products. This clay is specifically designed for polyolefin nanocomposites fabrication. Its basal distance is 24.2 Å. According to the supplier, Cloisite 20A is modified using an amount of monovalent cations of 95 meq/100 g. Taking into account the cationic exchange capacity of pristine sodic montmorillonite (92.6 meq/100 g), this means that all available cationic sites in Cloisite 20A are occupied by an organic cation without significant excess of this organic modifier. Before use, Cloisite 20A was dried in a vacuum oven at 60 °C for 48 h.

3. Composites preparation

The list of the composites prepared is given in Table 2. Composites extrusion was carried out using a Leistritz 18HP co-rotating twin-screw extruder ($L = 720$ mm; $D = 18$ mm; $L/D = 40$). The screw profile comprised three sequences of mixing elements (kneading blocks at 30° or 60° for dispersive mixing and kneading blocks at 90° for distributive mixing) separated by conveying zones. The detailed configuration is given elsewhere [23]. In a first step, polymer/Cloisite 20A masterbatches were extruded in a 3:1 ratio. The polymer and the organoclay were fed simultaneously at the main hopper to avoid the formation of macro-aggregates

[24]. The extrusion was carried out at 200 °C and 100 RPM through a circular die ($D = 2$ mm). The extrudate was pelletized. The exact concentration of organoclay in the resulting masterbatch was verified by thermogravimetric analysis (TGA). In a second step, the masterbatches were diluted in the matrix at the desired organoclay concentration. The matrix and the masterbatch were fed simultaneously at the main hopper. The extrusion was carried out in the same conditions as previously and the extrudate was pelletized. ASTM type I dog-bones specimens for tensile tests experiments were further injection-molded using a Sumimoto 500t electric press. The injection temperature was 200 °C and the mold temperature was kept at 30 °C.

4. Characterization

4.1. Clay dispersion

Clay dispersion in the composites was analyzed at the micro-scale using a FEG-SEM Hitachi S4700 scanning electron microscope (SEM) operating at 2 kV, and at the nanoscale using a Philips CM200 transmission electron microscope (TEM) operating at 200 kV. For SEM observation, the samples were polished using a series of polishing papers (abrasive: silicon carbide; grain size: 65–6 µm) and polishing cloths (abrasive: diamond powder; grain

Table 2

List and structural characteristics of the samples prepared.

Sample name	Composition			Micro-aggregates size (by SEM)		Tactoids size (by XRD and TEM ^a)				Exfoliated platelets (by TEM)	
	Matrix (wt.%)	Coupling agent (wt.%)	Clay (wt.%)	$\langle L_{\text{micro}} \rangle$ (µm)	$\langle t_{\text{micro}} \rangle$ (µm)	d_{001} (Å)	$\langle L_{\text{nano}} \rangle$ (nm)	$\langle t_{\text{nano}} \rangle$ (nm)	N	Density (%)	
HDPE	100	–	–	–	–	–	–	–	–	–	–
PNC5(HDPE)	95	–	5	<3.0	<1.0	24.5	Not evaluated	–	–	–	None (micro-composite)
LDPE	100	–	–	–	–	–	–	–	–	–	–
PNC5(LDPE)	95	–	5	<3.0	<1.0	24.8	Not evaluated	–	–	–	None (micro-composite)
LLDPE-4	100	–	–	–	–	–	–	–	–	–	–
PNC5(LLDPE-4)	95	–	5	<2.5	<1.0	31.5	Not evaluated	–	–	–	None (micro-composite)
LLDPE-6	100	–	–	–	–	–	–	–	–	–	–
PNC5(LLDPE-6)	95	–	5	<2.5	<1.0	31.8	Not evaluated	–	–	–	None (micro-composite)
LLDPE-8	100	–	–	–	–	–	–	–	–	–	–
PNC4(LLDPE-8) ^a	96	–	4	<2.5	<1.0	33.9	949 ± 581	173 ± 104	51.6	–	None (micro-composite)
PNC4(LLDPE-8/C ₁) ^a	84	12 (C ₁)	4	<1.0	<0.25	No peak	106 ± 52	10 ± 10	3.1	40	–
PNC4(LLDPE-8/C ₂) ^a	84	12 (C ₂)	4	<1.0	<0.25	44.2	163 ± 107	16 ± 13	4.4	41	–
PNC5(LLDPE-8)	95	–	5	<2.5	<1.0	27.9	Not evaluated	–	–	–	None (micro-composite)

^a A detailed analysis of clay micro- and nanodispersion is given elsewhere [17]. Tactoids size was determined from semi-quantitative TEM image analysis on a population of ca. 200 clay tactoids. The huge uncertainties are linked to the broad size distribution.

size: 3–0.5 μm). The polished samples were chemically etched using the procedure described by Bassett and Olley [25] in order to remove the amorphous phase and reveal the clay particles. This etching procedure facilitates the observation of the clay micro-particles without affecting the integrity of the sample. Observations were performed along two plans (A–A plan and B–B plan) as shown in Fig. 1. For TEM observation, the samples were ultra-microtomed at -100°C . In addition to the microscopic observations, the basal

Fig. 1. Schematics of the tensile test specimens. Tensile testing and injection directions are equivalent. Clay dispersion and structure were analyzed in the A–A and B–B plans. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

distance of the clay in the composites was determined by wide angle X-ray diffraction (WAXD) using a Bruker D8 Discover high resolution X-ray diffractometer operating at 40 kV and 40 mA (Cu K_α radiation). The spectra were obtained in reflexion mode between 0.8° and 10° , using a step increment of 0.015° and an acquisition time of 1.5 s/point.

4.2. Mechanical properties

Classical tensile tests were performed following ASTM D638 recommendations using an Instron 55R1123 testing machine at a crosshead speed of 50 mm/min. A displacement extensometer (gauge length: 50 mm; maximum travel distance: 5 mm) was used for the determination of the tensile modulus. For volume strain determination and acoustic emission testing, tensile tests were performed at a lower crosshead speed of 10 mm/min for enhanced sensitivity. Volume strain measurements were performed using an Instron Advanced Video Extensometer 2663-821 measuring the variations in length and width, coupled to a transverse strain sensor (maximum travel distance: 0.5 mm) measuring the variation in thickness. The volume strain is then given by:

$$\frac{\Delta V}{V_0} = (1 + \varepsilon_1)(1 + \varepsilon_2)(1 + \varepsilon_3) - 1$$

where ΔV is the change in volume, V_0 is the original volume, ε_1 is the axial strain and ε_2 and ε_3 are the strains in the width and thickness directions respectively. For HDPE and LDPE composites, acquisition was stopped at the onset of striction ($\varepsilon_1 \approx 15\%$): after this point, measurements were no longer uniform and therefore representative of the deformation of the material. For LLDPE composites, acquisition was performed up to an elongation of 30% (limit of the video extensometer) since the deformation was uniform throughout the test. Acoustic emission signals were recorded with an ultrasonic transducer Panametrics Accuscan A133S-RM operating at

Fig. 2. SEM images of polyethylene/clay composites prepared without coupling agent: (a) PNC5(HDPE); (b) PNC5(LDPE); (c) PNC5(LLDPE-8).

2.25 MHz. For HDPE and LDPE composites, measurements were performed until break point. For LLDPE composites, acquisition was stopped at an elongation of 100% due to the apparition of surface roughness, which induced too much noise in the measurements.

5. Results and discussion

5.1. Clay dispersion in the composites

The clay dispersion in the composites was analyzed by SEM, WAXD and TEM. Composites prepared without coupling agent essentially showed well distributed micro-aggregates oriented along the injection direction (Fig. 2). The average length $\langle L_{\text{micro}} \rangle$ and thickness $\langle t_{\text{micro}} \rangle$ of those micro-aggregates were $\sim 3 \mu\text{m} \times \sim 1 \mu\text{m}$ for PNC5(HDPE) and PNC5(LDPE), and $\sim 2.5 \mu\text{m} \times \sim 1 \mu\text{m}$ for PNC5(LLDPE-4), PNC5(LLDPE-6), and PNC5(LLDPE-8). At the nanoscale, TEM showed that PNC5(HDPE) and PNC5(LDPE) contained only clay micro-particles (Fig. 3). The basal distances, as recorded by WAXD, were respectively 24.5 Å and 24.8 Å, indicating the absence of significant intercalation during compounding (Fig. 4). Thus, PNC5(HDPE) and PNC5(LDPE) were classified in the category of conventional unintercalated microcomposites. PNC5(LLDPE-4), PNC5(LLDPE-6) and PNC5(LLDPE-8) were also found by TEM to be constituted mainly of clay micro-particles (Fig. 3). However, the basal distances recorded were respectively equal to 31.5 Å, 31.8 Å and 27.9 Å, indicating a good level of intercalation (Fig. 4). Therefore, PNC5(LLDPE-4), PNC5(LLDPE-6) and PNC5

(LLDPE-8) were classified in the category of intercalated micro-composites. A detailed analysis of clay dispersion in the composites prepared using a coupling agent (PNC4(LLDPE-8/C₁) and PNC4(LLDPE-8/C₂)) can be found elsewhere [17]: it includes WAXD spectra as well as SEM and TEM photographs. Briefly, those formulations were found to contain a small proportion of clay micro-particles of average length $\langle L_{\text{micro}} \rangle$ and thickness $\langle t_{\text{micro}} \rangle$ in the range of $\sim 1.0 \mu\text{m} \times \sim 0.25 \mu\text{m}$. In addition, they exhibited high levels of delamination at the nanoscale, with tactoids comprising a number N of 3–5 platelets per stack (depending on the grade of coupling agent) and a density of individually exfoliated platelets estimated to $\sim 40\%$. Therefore, the formulations PNC4(LLDPE-8/C₁) and PNC4(LLDPE-8/C₂) were considered as semi-exfoliated nanocomposites. A summary of the structural characteristics of the composites prepared is given in Table 2.

5.2. Mechanical properties of the composites

The mechanical properties of the various composites are summarized in Table 3. As expected from the coarse dispersion state of the clay, the microcomposites prepared without coupling agent only showed minor improvements in tensile modulus and yield strength. However, depending on the matrix type, they exhibited very different behaviors in elongation (Fig. 5). Upon tensile testing, PNC5(HDPE) and PNC5(LDPE) showed a fairly early striction at $\varepsilon_1 \approx 15\%$. In the case of PNC5(HDPE), the plastic deformation remained concentrated in the striction zone which extended until

Fig. 3. TEM images of polyethylene/clay composites prepared without coupling agent: (a) PNC5(HDPE); (b) PNC5(LDPE); (c) PNC5(LLDPE-8).

Fig. 4. WAXD spectra of polyethylene/clay composites prepared without coupling agent.

Table 3

Tensile properties of the composites at 50 mm/min: tensile modulus (E), yield strength at 2% offset ($\sigma_{2\%}$), elongation at break (ϵ_b), energy absorbed at break (E_b).

	E (MPa)	$\sigma_{2\%}$ (MPa)	ϵ_b (%)	E_b (J)
HDPE	1360 ± 73	20.2 ± 0.3	116 ± 6	31 ± 2
PNC5(HDPE)	1650 ± 121	22.3 ± 0.2	138 ± 20	28 ± 3
LDPE	204 ± 2	7.8 ± 0.1	104 ± 3	19 ± 1
PNC5(LDPE)	288 ± 7	7.9 ± 0.1	117 ± 8	22 ± 2
LLDPE-4	263 ± 4	6.9 ± 0.1	474 ± 20	72 ± 1
PNC5(LLDPE-4)	340 ± 10	7.1 ± 0.1	>911	>146
LLDPE-6	265 ± 4	6.9 ± 0.1	480 ± 21	77 ± 1
PNC5(LLDPE-6)	343 ± 11	7.1 ± 0.1	>911	>151
LLDPE-8	263 ± 4	7.4 ± 0.1	451 ± 4	75 ± 1
PNC4(LLDPE-8)	328 ± 14	7.6 ± 0.1	909 ± 4	>169
PNC4(LLDPE-8/C ₁)	341 ± 17	8.2 ± 0.1	536 ± 19	103 ± 13
PNC4(LLDPE-8/C ₂)	404 ± 13	8.9 ± 0.1	>911	>183
PNC5(LLDPE-8)	341 ± 8	7.4 ± 0.1	>911	>164

failure. The elongation at break increased by 19% compared to pure HDPE. In the case of PNC5(LDPE), most deformation concentrated in the striction zone. The elongation at break increased by 13% compared to pure LDPE. PNC5(LLDPE-4), PNC5(LLDPE-6) and PNC5(LLDPE-8) were found to behave in a very different manner. Tensile test specimens did not undergo striction but rather presented a homogeneous deformation. No failure was observed up

to an elongation of 911% (upper limit of the equipment). Therefore, for those specific microcomposites, the elongation at break was increased by more than 100% compared to pure LLDPE matrices. On the other hand, nanocomposites prepared using a coupling agent (PNC4(LLDPE-8/C₁) and PNC4(LLDPE-8/C₂)) exhibited significant enhancements in tensile modulus and tensile strength compared to the pure matrix due to the dispersion of the clay at the nano-scale. In addition, the elongation at break was found to increase compared to the pure matrix. This effect was particularly pronounced for PNC4(LLDPE-8/C₂) which again presented an increase in elongation at break higher than 100% compared to pure LLDPE-8.

Those results demonstrate that both LLDPE/clay micro- and nanocomposites exhibit a very peculiar behavior in deformation compared to HDPE/clay or LDPE/clay composites. In the range of clay concentrations tested, the presence of clay clearly improves the ductility of the material and therefore its toughness, as estimated from the energy absorbed during the tensile test.

5.3. Micro-mechanisms of deformation and failure

In order to elucidate the micro-mechanics of deformation of the various composites prepared, volume strain and acoustic emission measurements were coupled to tensile testing. Upon tensile testing of pure polymers, a zero volume strain variation indicates pure shear banding whereas an increase in volume strain is generally associated with the creation of voids [18]. Composites frequently

Fig. 5. Photographs of some tensile test specimens after drawing at 50 mm/min: (a) PNC5(HDPE); (b) PNC5(LDPE); (c) PNC5(LLDPE-8).

exhibit a higher volume strain than pure matrices due to the additional generation of voids by debonding at the polymer/filler interface [19–22]. The volume strain curves obtained in this work are given in Fig. 6. Within the elastic region ($\varepsilon_1 < 10\%$), the volume strain variation was found to be fairly low ($\Delta V/V_0 \approx 3\text{--}4\%$) for all matrices tested, indicating that the deformation of HDPE, LDPE and LLDPE-8 essentially proceeds by shear banding with limited voiding. The volume strain was systematically higher for the corresponding composites but remained low ($\Delta V/V_0 \approx 5\%$), thus demonstrating that in the elastic region, there is no significant voiding

resulting from the presence of the clay. Volume strain measurements carried out in the plastic region for LLDPE-8 confirmed the limited increase in volume strain ($\Delta V/V_0 \approx 9\%$ at $\varepsilon_1 = 30\%$), indicating that shear banding remains the dominant mode of deformation at high elongations, as considerably higher $\Delta V/V_0$ values are expected when voiding becomes dominant. Micro- and nanocomposites based on LLDPE-8 followed the same behavior than the matrix, showing that the incorporation of clay this polymer does not lead to important voiding in the plastic region. Interestingly, the volume strain increase was found to be higher for nanocomposites ($\Delta V/V_0 \approx 11\text{--}13\%$ at $\varepsilon_1 = 30\%$) than for microcomposites ($\Delta V/V_0 \approx 10\%$ at $\varepsilon_1 = 30\%$) which is indicative of more important voiding due to debonding at more numerous clay particles as a result of the finer clay dispersion.

Fig. 6. True tensile stress and volume strain variation during tensile testing at 10 mm/min: (a) HDPE and its microcomposite; (b) LDPE and its microcomposite; (c) LLDPE-8 and its micro- and nanocomposites.

Fig. 7. Cumulative number of acoustic events detected during tensile testing at 10 mm/min: (a) HDPE and its microcomposite; (b) LDPE and its microcomposite; (c) LLDPE-8 and its microcomposite.

Acoustic emission testing was also performed, allowing the detection of a number of acoustic events. In pure polymers, those events have been associated with cavitation [26]. In polymer/clay composites, the number of events is generally higher than for pure matrices and has been associated with debonding at the polymer/clay interface or fracture of the clay particles. Slipping of the clay layers and shear yielding are not expected to generate detectable signals [22]. Although the analysis of the individual acoustic events detected is difficult, the cumulative number of events detected during the deformation of the specimens can provide interesting information. This information is given in Fig. 7. In HDPE, an intermediate number of acoustic events were detected, starting at the onset of plastic region. In the corresponding PNC5(HDPE) microcomposite, a dramatic increase in the number of events detected was observed. Those events were mostly detected in the plastic region. In this case, acoustic emission testing provide complementary information to volume strain measurements, allowing to propose that significant debonding at the polymer/clay interface and/or fracture of the clay micro-particles takes place during plastic deformation of PNC5(HDPE). Meanwhile, a fairly low number of acoustic events were detected in LDPE, LLDPE-8 and their composites. Those results are in adequation with the volume strain measurements performed, confirming that there is almost no voiding in the pure LDPE and LLDPE-8 matrices, and that there is no significant debonding at the polymer/clay interface nor fracture of the clay micro-particles in their corresponding composites.

In order to confirm those conclusions, tensile test specimens drawn at 50 mm/min were carefully analyzed by SEM and TEM and compared to undrawn specimens. The case of the microcomposites was first considered. In drawn PNC5(HDPE), SEM showed a high level of porosity together with severe decohesion at the clay

micro-particles (Fig. 8). In addition, TEM showed numerous cracks of length higher than 1 μm originating either in the polymer matrix or at the polymer/clay interface (Fig. 9). The microstructure was very different for drawn specimens of PNC5(LDPE) and PNC5(LLDPE-8). In those microcomposites, clay micro-particles were found by SEM and by TEM to exhibit a higher aspect ratio than in the undrawn materials, suggesting an elongation of the clay micro-particles during the test (Figs. 10–12). The deformation of the clay micro-particles is very clear when comparing Fig. 10 (drawn material) and Fig. 2 (undrawn material): in the drawn materials, the clay micro-particles have an average thickness $\langle t_{\text{micro}} \rangle$ lower than 0.5 μm . This phenomenon is observed in both PNC5(LDPE) and PNC5(LLDPE-8), but is more pronounced in the latest microcomposite. No extensive debonding at the polymer/clay interface was observed by SEM for PNC5(LDPE) nor for PNC5(LLDPE-8). In PNC5(LLDPE-8), a few micro-cracks could be observed by TEM, mostly originating at the polymer/clay interface. However, contrarily to the case of PNC5(HDPE), those micro-cracks generally remained limited in size ($<1 \mu\text{m}$) and did not propagate significantly in the matrix (Fig. 12). Finally, in the drawn nanocomposites PNC4(LLDPE-8/C₁) and PNC4(LLDPE-8/C₂), a significant elongation of the clay micro-particles was observed by SEM, similarly to the case of the PNC5(LLDPE-8) microcomposite (Fig. 13). At the nanoscale, no evidence of debonding at the polymer/clay interface was observed and no micro-crack could be detected (Fig. 14). In Fig. 14, it can be noted that the clay platelets in the drawn nanocomposites present a zig-zag structure. We attribute this specific feature to a reorganization of the flexible clay platelets upon fast elastic recovery following either the rupture (PNC4(LLDPE-8/C₁)) or the removing of the unbroken specimen from the clamps (PNC4(LLDPE-8/C₂)).

Fig. 8. SEM micrographs of PNC5(HDPE) drawn at 50 mm/min: (a) void formation by debonding at the polymer/clay interface in the bulk material; (b) fibrillation and debonding at the polymer/clay interface on the external surface of the tensile test specimen.

Fig. 9. TEM images of PNC5(HDPE) drawn at 50 mm/min: (a) overview and (b) high magnification (on this specific picture, micro-cracks are highlighted by arrows).

Fig. 10. SEM micrographs of PNC5(LDPE) (a) and PNC5(LLDPE-8) and (b) drawn at 50 mm/min (bulk material).

5.4. Discussion

The combination of volume strain measurements, acoustic emission testing and electron microscopy allows us to draw several conclusions regarding the micro-mechanisms of deformation in polyethylene/clay composites. Within the elastic region, the presence of clay does not seem to affect the deformation mechanisms of the material, as shown by volume strain and acoustic emission measurements. Major differences occur in the plastic region. The case of the microcomposites will be considered first. HDPE/clay microcomposites were shown to exhibit important voiding mainly resulting from severe debonding at the polymer/clay interface, in addition to the conventional shear banding and

voiding inherent to the pure HDPE matrix. Meanwhile, the main mode of deformation in LDPE/clay and LLDPE/clay microcomposites was found to be shear banding, resulting in the elongation of the clay micro-particles. The mechanism proposed to explain the deformation of the clay micro-particles is illustrated in Fig. 15. Upon tensile testing, the clay platelets closer to the polymer/clay interface are dragged into the tensile test direction by the polymer chains in motion. The movement is transferred along the transverse direction from the clay platelets closest to the interface to furthest clay platelets via slipping, leading to an overall elongation of the clay micro-particles. This mechanism is more likely to occur for strong interfaces (no-slip boundary condition), but it may also occur for medium to weak interfaces (such as those expected for

Fig. 11. TEM images of PNC5(LDPE) drawn at 50 mm/min (bulk material). Some micro-cracks are indicated by arrows.

Fig. 12. TEM images of PNC5(LLDPE-8) drawn at 50 mm/min (bulk material): (a) overview and (b) details of micro-cracks formation inside a clay micro-particle and by debonding at the polymer/clay interface.

polyethylene/clay microcomposites prepared without coupling agent) since the clay micro-particles are submitted to compression forces in the transverse directions during the test, ensuring contact at the polymer/clay interface. In LLDPE/clay microcomposites, a few micro-cracks were also detected by electron microscopy. Most of them were initiated by debonding at the polymer/clay interface

but did not propagate significantly in the test specimen. Indeed, LLDPE is well known for its high fracture toughness (J_c) [27,28] which is defined as the ability of a material containing a crack to resist fracture. Mirabella et al. [28] have reported J_c values of 29 kJ/m² for LLDPE against values comprised between 1.0 and 2.0 kJ/m² for LDPE or HDPE of similar molecular weight. Therefore,

Fig. 13. SEM images of the nanocomposites PNC4(LLDPE-8/C₁) (a) and PNC4(LLDPE-8/C₂) (b) drawn at 50 mm/min (bulk material).

Fig. 14. TEM images the nanocomposites (bulk material) before and after drawing at 50 mm/min: (a) PNC4(LLDPE-8/C₁) and (b) PNC4(LLDPE-8/C₂).

it is believed that the micro-cracks eventually formed in LLDPE/clay microcomposites do not propagate catastrophically in the matrix due to its inherent toughness. This, in addition with the dissipation of energy via the deformation of the clay micro-particles upon shear banding, would explain the extraordinary toughness of LLDPE/clay microcomposites compared to LDPE/clay and HDPE/clay microcomposites.

The role of clay dispersion on the deformation of the composites is still unclear. In PNC4(LLDPE-8/C₁) and PNC4(LLDPE-8/C₂), the micro-dispersed fraction of clay was found to behave in the same

manner as in the microcomposites, with clay micro-particles experiencing an overall elongation upon tensile testing. However, it was not possible to draw clear conclusions regarding the fraction of clay dispersed at the nanometric scale in the form of intercalated tactoids or individual platelets. Volume strain measurements indicated that voiding was slightly higher in nanocomposites than in microcomposites. In polymer/clay composites, voiding by debonding at the polymer/clay interface should result from a balance between the interfacial area involved and the adhesion at the polymer/clay interface. PNC4(LLDPE-8/C₁) and PNC4(LLDPE-8/C₂)

Fig. 15. Proposed mechanism for clay micro-particles deformation upon tensile testing in PNC5(LLDPE) and PNC5(LLDPE-8) microcomposites: (a) clay micro-particles in undrawn microcomposites and (b) clay micro-particles upon tensile testing: the platelets closest to the polymer/clay interface are dragged by the polymer chains in motion; as the movement is transferred to furthest clay platelets via slipping, the overall aspect ratio of the clay micro-particles increases.

present very similar dispersion states, as shown by the semi-quantitative image analysis of the clay tactoids (Table 2). However, we reported in a previous work [17] that the polar component of the surface energy (γ_s^p) was 1.0 mN/m for the maleated coupling agent C₂ against 0.5 mN/m for C₁ (as a comparison, this value was equal to 0.08 mN/m for the unmodified LLDPE-8 resin). As a consequence, it was concluded that C₂ might be able to produce stronger polar interactions with Cloisite 20A than C₁, resulting in stronger interactions at the polymer/clay interface. The higher volume strain increase measured for PNC4(LLDPE-8/C₁) compared to PNC4(LLDPE-8/C₂) tends to support this conclusion. However, this could not be confirmed by electron microscopy since no significant difference in structure was detected between the two nanocomposites. Finally, if the reorganization of the clay micro-particles upon tensile testing has been well established in this work in both microcomposites and nanocomposites of LLDPE, a possible reorganization of the fraction of clay dispersed at the nanometric scale in the nanocomposites cannot be excluded. Indeed, in latex nanocomposites containing well dispersed silica nanoparticles, Rharby et al. [29] have shown a significant reorganization of the filler structure under deformation using small angle neutron scattering (SANS). The fillers were found to reorganize by localized shear displacements. The authors suggested that those reorganizations could dissipate some of the energy stored in the material, and in this way contribute to delay crack propagation. Gersappe [30] validated their hypothesis through molecular dynamics simulations and showed that the mobility of the nanoparticles, which increases as the filler size decreases and as the interfacial strength increases, controlled the ability of the nanocomposite to dissipate energy. However, the methods used in this work did not allow us to confirm such a reorganization.

6. Conclusions

In this work, the mechanical properties in tension of several polyethylene/clay micro- and nanocomposites were examined with emphasis on elongation at break and toughness. The micro-mechanisms of deformation upon tensile testing were investigated and related to the matrix characteristics and the dispersion state of the clay. In HDPE/clay microcomposites, the dominant mode of deformation was found to be voiding by debonding at the polymer/clay interface, resulting in crack formation and propagation. In LDPE/clay and LLDPE/clay microcomposites, the dominant mode of deformation was shear banding, inducing a deformation of the clay micro-particles. It is believed that the extraordinary increase

in ductility observed in LLDPE/clay microcomposites is related to: (i) the dissipation of energy via the reorganization of the clay micro-particles, and (ii) the dissipation of energy via debonding at the polymer/clay interface, generating some micro-cracks that do not propagate in the matrix due to the high fracture toughness of LLDPE. The effect of the clay dispersion on the elongation at break of polyethylene/clay composites is still unclear. In LLDPE/LLDPE-g-MA/clay nanocomposites, more voiding was measured than in LLDPE/clay microcomposites. This was attributed to a higher polymer/clay interfacial area counterbalancing for the better adhesion at the interface. However, electron microscopy did not enable the direct visualization of voiding. Although it could not be demonstrated with the experimental techniques used in this work, a possible reorganization of the clay exfoliated platelets during shear banding cannot be excluded for LLDPE/LLDPE-g-MA/clay nanocomposites.

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