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# DEFORMATION AND FRACTURE MECHANISMS IN POLYETHYLENE / CLAY NANOCOMPOSITES

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## Abstract

Polyethylene/montmorillonite nanocomposites based on LDPE, HDPE and LLDPE of similar rheological properties were prepared and mechanically tested in tension mode. It was shown that nanocomposites based on LLDPE exhibit a very peculiar behavior, with a significant improvement in toughness (elongation at break). The microstructural features of the various nanocomposites were investigated through scanning and/or transmission electron microscopy. Based on those observations, an explanation for the deformation and fracture mechanisms in LLDPE/montmorillonite nanocomposites was proposed.

## Introduction

Layered silicate-based polymer nanocomposites have attracted considerable interest since nanometric scale dispersion was obtained in polyamide/clay composites [1]. When compared with conventional micro-fillers, the incorporation of layered silicates in polymeric matrices can lead to remarkable properties, resulting in material valorization at moderate cost [2]. Montmorillonite, a natural clay with an aspect ratio higher than 100, is frequently used as a reinforcement for polymer nanocomposites. Compared to the pure polymer, polymer/montmorillonite nanocomposites exhibit a significant increase in mechanical properties such as elastic modulus and ultimate strength. This effect is even more pronounced when the clay forms an exfoliated rather than an aggregated or an intercalated structure. However, it has generally been observed that the incorporation of montmorillonite in polymers results in a reduction of the elongation at break. Based on our knowledge, only few studies have reported an increase in the elongation at break for polyolefin/clay nanocomposites. Zhang and Sundararaj [3] observed an increase of about 50% in elongation at break for LLDPE/clay (5%wt.) nanocomposites compatibilized with a coupling agent (LLDPE grafted with maleic anhydride: LLDPE-g-MAH). They attributed this particular behavior to the formation of strong polymer/clay interfaces resulting from the addition of the coupling agent. Stoeffler et al. [4] has recently reported an increase in elongation at break of more than 100% for both LLDPE/clay (4%wt.) and LLDPE/LLDPE-g-MAH/clay (4%wt.) nanocomposites. Those results indicate that the interfacial strength is not the only factor responsible for the increase in toughness. Thus, clay nanocomposites prepared

from LLDPE seem to exhibit a very peculiar tensile deformation behavior.

In this work, the clay dispersion and the tensile properties of uncompatibilized clay nanocomposites based on LDPE, LLDPE and HDPE having similar molecular weights and rheological properties were investigated. The deformation process of those nanocomposites was analyzed through SEM and TEM characterization. An explanation for the peculiar behavior of LLDPE/clay nanocomposites was then proposed.

## Materials

Three grades of polyethylene (LDPE, LLDPE and HDPE) having a melt flow index of ~1g/10min (190°C/2.16kg) were selected for the study. Their characteristics are summarized in Table 1. These polymers were kindly provided by Nova Chemicals. The nanofiller, dimethyl dihydrogenated tallow ammonium modified montmorillonite (Cloisite 20A), was purchased from Southern Clay Products. Before utilization, the Cloisite 20A was dried in a vacuum oven at 60°C for 48 h.

## Nanocomposites Preparation

Nanocomposites containing 5%wt. of Cloisite 20A were extruded using a Leistritz 18HP co-rotating twin-screw extruder (L=720mm; D= 18mm; L/D= 40). The screw profile comprised 3 mixing zones composed of dispersive and distributive mixing elements. The extrusion was carried out at 200°C and 100RPM through a circular die (D=2mm) and the extrudate was further pelletized. Type I dog-bone specimens for tensile tests experiments were injection-molded from the pellets obtained using a Sumimoto 500t electric press operated at 200°C. In this article, the polymer nanocomposites are labeled PNC5 (matrix).

## Characterization

### Clay Dispersion

The clay dispersion and its microstructure in the nanocomposites were analyzed at the micro- and nano-scales using a Hitachi S4700 field emission gun scanning electron microscope (SEM) operating at 2kV and a Philips



CM200 transmission electron microscope (TEM) operating at 200kV. For SEM observation, the samples were cryo-microtomed or polished, and chemically etched [5]. For TEM observation, the samples were cryo-ultramicrotomed. In addition of the microscopic observations, the basal distance in the nanocomposites was determined by wide angle X-ray diffraction (WAXD) using a Bruker D8 Discover high resolution X-ray diffractometer operating at 40kV and 40mA (CuK $\alpha$  radiation).

## Mechanical Properties

Tensile tests were performed at room temperature using an Instron 55R1123 testing machine according to ASTM D638 procedure using type I specimen. The tensile modulus and elongation at break were measured at 50mm/min. An extensometer (50mm; 10% deformation) was used for the deformation measurement and determination of the tensile modulus.

## Results and Discussion

### Clay Dispersion in Nanocomposites

The clay dispersion in nanocomposites was analyzed by XRD, SEM and TEM. The XRD spectra seem to indicate that the PNC5(LDPE), PNC5(HDPE) and PNC5(LLDPE) are mostly intercalated, with respective basal distances of 24.8Å, 24.5Å and 27.9Å (Figure 1). At the micro-scale, SEM photographs show the presence of well distributed micro-aggregates oriented along the injection direction for all composites. The average length of those micro-aggregates is 3  $\mu$ m and their thickness is  $\sim$ 1  $\mu$ m (Figure 2). The nano-structure was analyzed by TEM which confirms the presence of tactoids in all formulations, in accordance with XRD results. PNC5(LDPE) and PNC5(LLDPE) contain tactoids in the range of 0.5 $\mu$ m to 2 $\mu$ m in length; on the contrary, PNC5(HDPE) contains bigger tactoids in the range of 1 $\mu$ m to 4 $\mu$ m in length (Figure 3).

### Mechanical Properties

The Young modulus and elongation at break of the nanocomposites are summarized in Table 2. Since all nanocomposites exhibit raw clay dispersion, it is not surprising that the Young modulus is only increased by  $\sim$ 40%, 30% and 20% for the formulations respectively based on LDPE, LLDPE and HDPE. However, it is interesting to observe the behavior in tension of those materials. Upon tensile testing, PNC5(LDPE) and PNC5(HDPE) show a rapid striction followed by failure: the elongation at break is increased by  $\sim$ 15% and  $\sim$ 20% compared to their respective matrices. The case of PNC5(LLDPE) is very different: test specimens do not show any striction but rather present an affine deformation. No failure was observed at an elongation level of 900% (upper limit of the equipment), meaning that the elongation

at break is increased by more than 100% compared to neat LLDPE.

### Micromechanics of Deformation and Rupture

In order to understand the micromechanics of deformation of the different polyethylene based nanocomposites, drawn test specimens were carefully analyzed by SEM and TEM. The bulk material was observed by SEM. SEM pictures reveal that for PNC5(LDPE) and PNC5(LLDPE), clay particles have been highly oriented during the test: they are extended and present a higher aspect ratio than in the undrawn nanocomposites. In addition, no significant decohesion is observed (Figure 4 a) and b)). Those observations indicate that upon testing, the micrometric clay particles have the ability to deform. It is probable that the clay platelets closer to the interface are dragged by the elongating polymer chains, transferring their movement to furthest clay platelets through a sliding process. This leads to an overall deformation and elongation of the tactoids. On the contrary, PNC5(HDPE) shows a very different aspect: the bulk nanocomposite is very porous and exhibits ductile deformation accompanied by cavitation around non deformed clay particles (Figure 4 c)).

At the nanoscale, the deformation mechanisms were investigated by TEM (Figure 5). In PNC5(LDPE) and PNC5(LLDPE), micro-cracks can be observed in the vicinity of clay particles. They mostly originate from decohesion at the polymer/clay interface. In PNC5(LLDPE), TEM also confirms the elongation of the clay tactoids upon testing. In PNC5(HDPE), observations do not show any significant elongation of the clay tactoids. However, microcracks are numerous and can reach several micrometers. They originate either in the bulk material or at a polymer/clay interface with a high amount of decohesion around clay particles.

### Discussion

The fracture toughness of LLDPE is considerably higher than LDPE or HDPE, as shown by the tensile tests performed. For resins of similar molecular weights, Mirabella et al. [6] have reported a fracture toughness value ( $J_c$ ) of 29 kJ/m<sup>2</sup> for LLDPE, against values comprised between 1.0 and 2.0 kJ/m<sup>2</sup> for LDPE and HDPE. Taking into account this information, and considering the micro and nanostructural features observed by SEM and TEM on the drawn samples, our hypothesis is that the important toughness increase observed in LLDPE nanocomposites is related to the inherent toughness of LLDPE. In the nanocomposites based on LLDPE and during tensile testing, energy appears to be dissipated through the deformation of clay tactoids and through the creation of free surfaces by decohesion at the polymer/clay interface. The microcracks created then propagate in the bulk polymer in the vicinity of the clay particles. However,



microcrack propagation in the polymer matrix rapidly stops, probably as a result of the inherent toughness of LLDPE. On the contrary, in LDPE and HDPE based nanocomposites, when a micro-crack is formed, its propagation is rapid and catastrophic due to the low toughness of those materials. It is highly probable that clay dispersion also affects the deformation and fracture behavior of those nanocomposites. The role of clay dispersion on those mechanisms is currently investigated and will be the subject of further work.

### Conclusions

This work shows that the addition of montmorillonite (~5%wt.) in LLDPE leads to a significant increase in toughness, which is not observed in nanocomposites based on LDPE or HDPE having similar rheological properties. This increase in toughness is observed even in the absence of a coupling agent. We attribute this peculiar behavior to the inherent toughness of LLDPE, which prevents the microcracks created during the tensile testing from propagating catastrophically within the matrix. Further

work is currently carried out to investigate the effect of clay dispersion on the deformation and rupture mechanisms in LLDPE/montmorillonite and LLDPE/LLDPE-g-MAH/montmorillonite nanocomposites.

### References

1. T. Kurauchi, A. Okada, T. Nomura, T. Nishio, S. Saegusa, and R. Deguchi, *S.A.E. Tech. Pap. Ser.*, **100**(5), 571 (1991).
2. S. Sinha Ray and M. Okamoto, *Prog. Polym. Sci.*, **28**, 1539 (2003).
3. M. Zhang and U. Sundararaj, *Macromol. Mater. Eng.*, **291**, 697 (2006).
4. K. Stoeffer, P. G. Lafleur, J. Denault, *Polymer Engineering and Science*, **48**(12), 2459-2473 (2008).
5. D.C. Bassett and R.H. Olley, *Polymer*, **25**, 935 (1984).
6. F.M. Mirabella Jr., S.P. Westphal, P.L. Fernando, and E.A. Ford, *Journal of Polymer Science: Part B: Polymer Physics*, **26**, 1995-2005 (1988).

Table 1. Properties of the polyethylenes.

Resin	MFI @ 190°C/2.16kg (g/10min)	$\rho$ (g/cm <sup>3</sup> )	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	M <sub>w</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>	Additives <sup>c</sup>
LDPE	0.75 <sup>a</sup>	0.919 <sup>a</sup>	-	-	-	-	PS
LLDPE	1.0 <sup>a</sup>	0.920 <sup>a</sup>	107 <sup>b</sup>	120 <sup>b</sup>	103300 <sup>a</sup>	3.33 <sup>a</sup>	PS
HDPE	1.2 <sup>a</sup>	0.960 <sup>a</sup>	-	-	-	-	PS

<sup>a</sup> Data from supplier.

<sup>b</sup> Determined using a TA Instruments DSC Q1000 (10°C/min).

<sup>c</sup> PS : process stabilizer.

Table 2. Tensile properties of the nanocomposites.

	Tensile modulus E (MPa)	Elongation at break $\epsilon$ (%)
LDPE	204±2	104±3
PNC5(LDPE)	288±7	117±8
LLDPE	263±4	476±20
PNC5(LLDPE)	341±8	>900
HDPE	1360±73	116±6
PNC5(HDPE)	1650±121	138±20

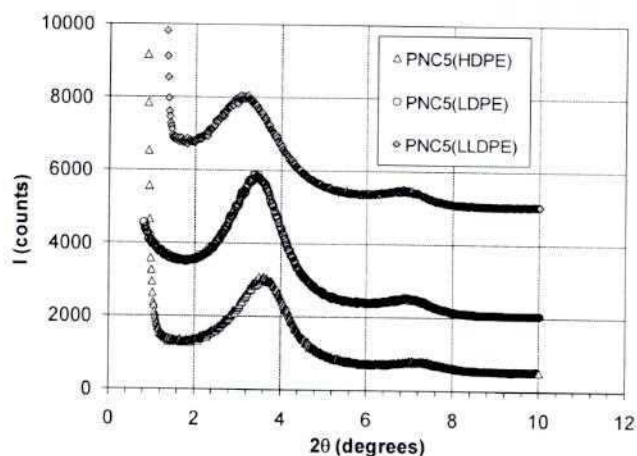


Figure 1. XRD spectra of the undrawn nanocomposites.

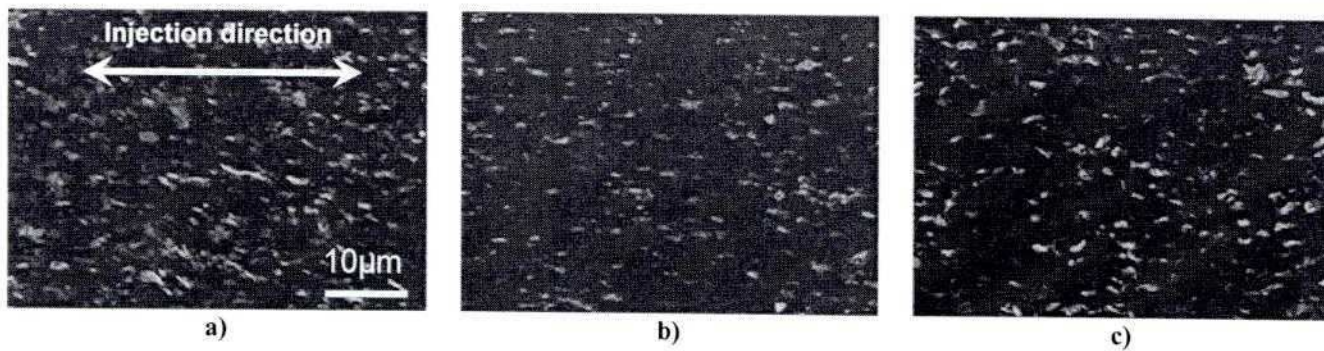


Figure 2. SEM micrographs of undrawn nanocomposites (bulk material): a) PNC5(LDPE); b) PNC5(LLDPE); c) PNC5(HDPE).

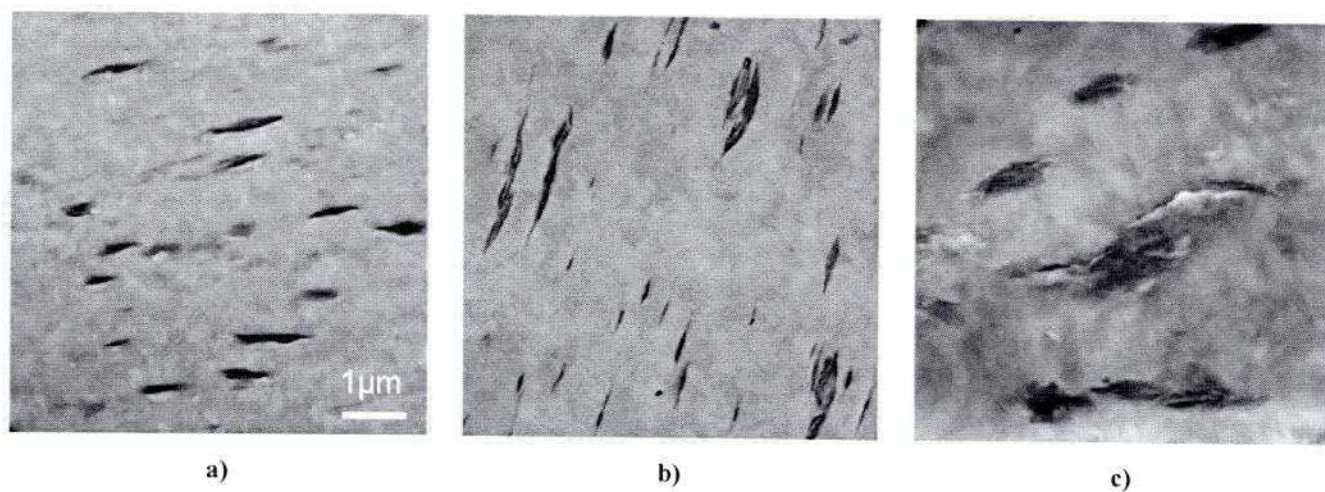


Figure 3. Clay dispersion in the bulk undrawn nanocomposites: a) PNC5(LDPE); b) PNC5(LLDPE); c) PNC5(HDPE).

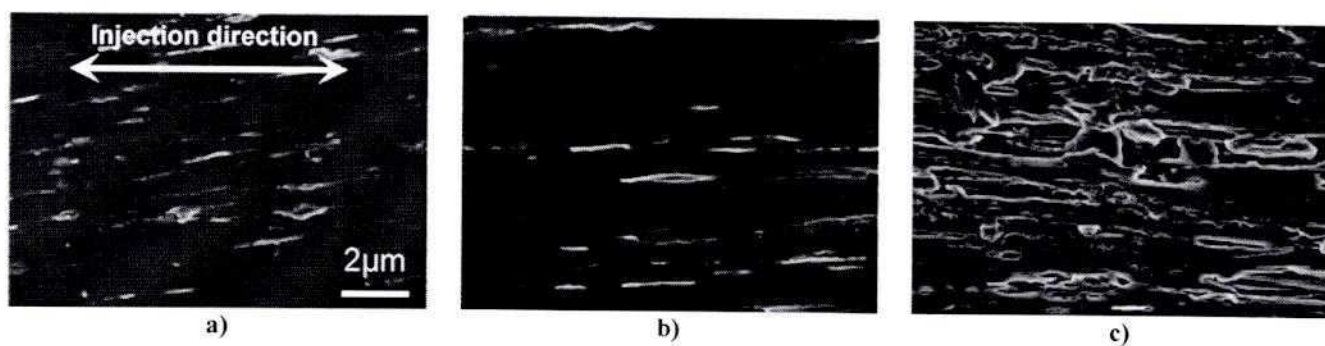


Figure 4. SEM micrographs of polished/etched nanocomposites drawn at 50mm/min (bulk material): a) PNC5(LDPE); b) PNC5(LLDPE-8); c) PNC5(HDPE).



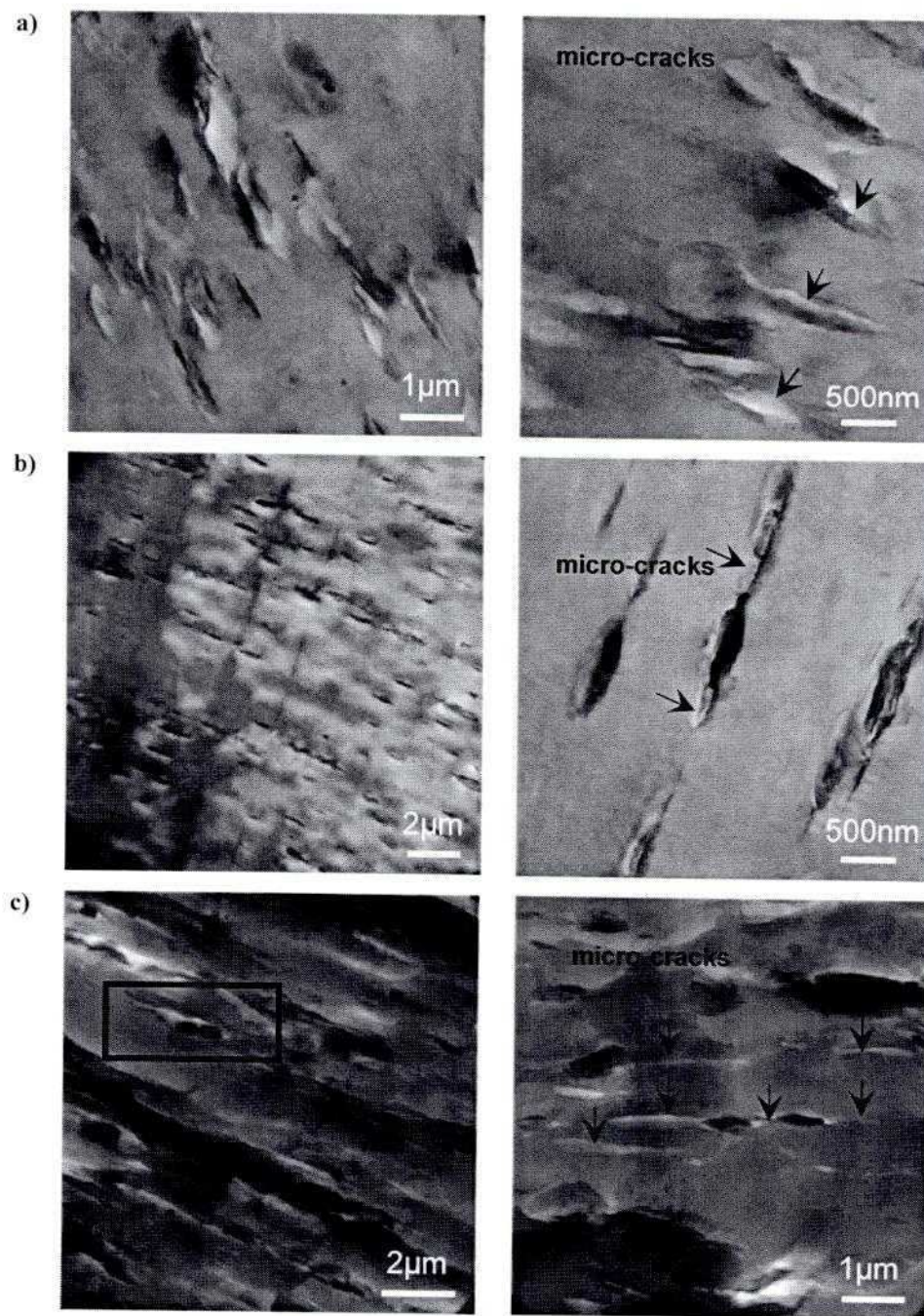


Figure 5. Deformation at the nanometric scale in the nanocomposites drawn at 50mm/min: a) PNC5(LDPE); b) PNC5(LLDPE); c) PNC5(HDPE).