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Essential work of fracture and failure mechanisms of polypropylene–clay nanocomposites

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Abstract

The fracture behavior of polymer nanocomposites (PNCs) based on a polypropylene with organo-modified clays (2 wt.%) and different coupling agents was studied by means of essential work of fracture (EWF). The PNC microstructure was characterized by clay particle dispersion at the micron scale ($>1\ \mu\text{m}$) and sub-micron scale (200 nm to $1\ \mu\text{m}$), with good intercalation and partial exfoliation ($<100\ \text{nm}$). Tensile testing showed significant improvements (+25–50%) corresponding to nanoparticle reinforcement effects. Fracture surfaces revealed that fracture occurred by void initiation at larger clay particles, followed by void growth and coalescence as the surrounding matrix stretched into ligaments. EWF improvements (+20%) were noted for PNCs that had fewer micron scale particles and showed higher tensile improvements. Toughness improvements were attributed to higher voiding stresses and improved matrix resistance attributed to finer, more oriented clay nanoparticles.

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Keywords: Polypropylene nanocomposites; Microstructure; Essential work of fracture; Toughness; Fractography

1. Introduction

PNCs with natural or synthetic layered silicates have been the object of several studies in the last decade. Provided that the layered silicates are dispersed, or exfoliated, at the nanometric scale within the polymer matrix, these PNCs are claimed to present significantly improved mechanical properties, namely Young's modulus or yield stress improved by 30–50% at clay contents as low as 2–5 wt.%. As described by micro-mechanical models, like that of Halpin and Tsai [1], these increases in Young's modulus are due to the extraordinarily high volume density ($\approx 10^{10}$ particles/ mm^3), the high aspect ratio (≥ 100) and the high modulus ($\approx 170\ \text{GPa}$) of these nanoparticles. As described by Cox's shear lag model [2], the strength improvements are due to this nanoparticle dispersion and to a hopefully strong interaction between the matrix and the nanoparticles, which accounts for the load-transfer effectiveness at the particle–matrix interface. Additional strength improvements could be related to an increased yield stress caused by the loss of mobility of the supermolecular

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Nomenclature

PNCs	polymer nanocomposites
PP	polypropylene
MAGPP	maleic anhydride grafted PP
XRD	X-ray diffraction
TEM	transmission electron microscopy
K_{Ic}	stress intensity factor
G_{Ic}	strain energy release rate
EWf	essential work of fracture
M_w	molecular weight
LMW	low molecular weight
IMW	intermediate molecular weight
HMW	high molecular weight
TSE	twin-screw extruder
FEGSEM	field-emission gun scanning electron microscope
2θ	X-ray diffraction angle
d_{001}	clay interlayer spacing
W_f	total work of fracture
W_p	non-essential work of fracture
l	ligament length
t	ligament thickness
β	shape factor
w_t	specific total work of fracture
w_e	essential specific work of fracture
βw_p	non-essential specific work of fracture
$w_{e,init}$	essential specific work of fracture at crack initiation
$(\beta w_p)_{init}$	non-essential specific work of fracture at crack initiation
$w_{e,prop}$	essential specific work of fracture at crack propagation
$(\beta w_p)_{prop}$	non-essential specific work of fracture at crack propagation
DDENT	deeply double edge-notched tension
E	Young's modulus
S_y	yield stress
r^2	least-squares regression squared correlation coefficients

structure of the polymer in the presence of fully exfoliated silicate nanoparticles due to the adsorption of polymeric chains on the nanoparticle surface [3]. Such an effect would however be accompanied by an increase in brittleness, as often observed in PNCs [4].

In recent years, specific efforts have been devoted to the development of melt-compounded polypropylene (PP) based PNCs with organically modified natural clay (montmorillonite) in which coupling agents, such as maleic-anhydride-grafted PP (MAGPP), were used to improve both the clay particle dispersion and particle–matrix adhesion. These PNCs contained typically 1–5 wt.% clay (sometimes more) with a coupling-agent-to-clay ratio of 1:1 and 2:1. In general, these non-exfoliated, well-intercalated PNCs led to improvements of 10–100% in Young's modulus, but yield stress improvements were not as high (e.g., $\leq 25\%$) [5]. It should be mentioned that the highest properties were obtained for high loadings of clay and coupling agents, often at a coupling-agent-to-clay ratio of 2:1. These increased properties were thus obtained at a significantly higher price, which reduces their range of application, for example, in the automotive sector. Evidence provided in terms of mechanical properties corresponded to micro-mechanical effects of conventional micro-composites, i.e., particle–matrix load-transfer improved by a coupling agent. In most cases, the impact resistance of the PP/clay composite decreased when an effective coupling agent was used, especially at high clay concentrations.

However, recent studies in PNCs have generally focused on rigidity and strength, and often neglected fracture resistance. When addressed, fracture resistance is generally studied through impact (Izod or Charpy) testing, which lacks the fundamental basis to be related to physical phenomena. Indeed, ASTM Izod and Charpy standards recommend that these methods be reserved for quality control and materials specification and should not be used to study the fracture behavior of a material. Also, the analysis of the mechanical behavior of PNCs, including impact or fracture, too often does not consider all particle-related features of the material, e.g., the presence of clay particles above 1 μm in size, and only takes into account intercalation and exfoliation levels from X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. While these two techniques reflect the nanodispersion of clay particles and cannot be discounted, they fail to represent what could be referred to as micro-dispersed clay particles (i.e., 0.5 μm and above), which are well known to affect fracture toughness in filled polymers (e.g., talc, calcium carbonate, etc.). Another particle-related feature often neglected is the crystalline morphology, especially the size and form of crystals, known to influence the fracture behavior of semi-crystalline polymers. Finally, the elasto-plastic behavior and fairly high ductility of PP-based PNCs makes fracture toughness characterization more complicated to perform; methods based on J -integral, stress intensity factor (K_{Ic}) and strain energy release rate (G_{Ic}) are generally not valid since plane strain conditions are difficult to obtain for these materials.

Recently, the fracture behavior of PNCs has been studied by means of the essential work of fracture (EWF) method [4,6,7]. The EWF test [8] is a means of separating the work associated with the fracture of a specimen into two components: one, designated as the EWF, that is intrinsic to the fracture of the material, and the other, designated as non-EWF, that is related to plastic work dissipation in the process zone, and depends upon the geometry of the specimen and process zone. This EWF test was first developed for thin metallic specimens and has become increasingly popular to determine the toughness of ductile polymers [9], especially different forms of PP-based materials, including blends and fiber-reinforced composites. This characterization method is attractive for materials presenting a significant amount of plasticity because it does not require the suppression of crack tip plasticity, contrary to the other mentioned means of measuring toughness, and therefore allows the use of thinner specimens ($\leq 1\text{--}2\text{ mm}$). The application of this method was recently reviewed for PNCs [6] where fracture energy was divided into a crack initiation term and a crack propagation term, after a method proposed by Mouzakis and Karger-Kocsis [10] and Hashemi and Williams [11].

A study on the fracture toughness of a MAGPP/clay PNC based on the essential work of fracture (EWF) method was recently reported [4]. This study revealed extensive void formation at clay particles in the micron or sub-micron range with limited fibrillation of the matrix. As a result, the fracture toughness decreased upon clay addition. These voids, as PNCs are further strained, grow through shear deformation, leave unbroken material that stretches into ligaments and eventually break in cascade, leading to failure. This series of events led to dramatic reduction in fracture toughness in uncoupled PP/clay PNCs. Using a coupling agent in PP/clay PNCs proved to improve clay intercalation, dispersion and interfacial interaction, and led to improvements in the fracture toughness with respect to their uncoupled version, but only up to the toughness levels of PP. Thus, although a relationship exists between clay particle dispersion, particle–matrix interactions and general modulus improvements, the details of this relationship, and more importantly, the key to high fracture toughness, are not fully understood. The objectives of this work thus are to describe the microstructure of PP-based PNCs, to relate it to their fracture toughness, and, by using EWF, to understand the sequence of events that lead to the fracture of PNCs.

2. Experimental

2.1. Materials and sample preparation

The polymer nanocomposites studied were formulated and fabricated as described in a previous publication [12]. The matrix used was polypropylene (Pro-fax PDC 1274 from Basell). Two types of organo-modified montmorillonite clay from Southern Clay Products were used: both modified with dimethyl di(hydrogenated tallow) quaternary ammonium, one with an excess amount of intercalant (Cloisite® 15A, designated as 15A for short), and the other with no excess (Cloisite® 20A, designated as 20A). PNCs with 2 wt.% of clay were prepared. Three commercially available MAGPPs with a low amount of grafted MA were used as coupling

Table 1
Designation of the materials studied

Material	Coupling agent	Clay
PP	–	–
PP/clay	–	15A
L-PNC1	LMW	15A
L-PNC2	LMW	20A
I-PNC1	IMW	15A
I-PNC2	IMW	20A
H-PNC1	HMW	15A
H-PNC2	HMW	20A

agents: one with a low molecular weight ($M_w = 56$ kg/mol), designated as LMW, one with an intermediate molecular weight ($M_w = 195$ kg/mol), designated as IMW, and one with a high molecular weight ($M_w = 330$ kg/mol), designated as HMW. PNC compounds were prepared by mixing equal amounts of coupling agent and organo-clay along with the required amount of PP in a twin-screw extruder (TSE). The designation of the materials studied is presented in Table 1.

Extruded pellets of PNCs were then injection-molded into ASTM D638 type I 3-mm thick dogbones for tensile testing and 25-mm wide, 80-mm long and 3-mm thick plates. The plates were reduced in thickness by compression molding to obtain 1-mm thick plates for the EWF fracture tests. Compression molding was done at 1 MPa as soon as the temperature of the plates reached 200 °C, and was followed by rapid cooling at 40 °C/min while maintaining pressure.

2.2. Microstructural characterization

Microstructural characterization of PNCs was performed through XRD analyses, TEM, and field emission gun scanning electron microscopy (FEGSEM). XRD analyses were done using a Bruker Discover 8 diffractometer operating at 40 kV and 40 mA with CuK_α radiation in the Bragg–Brentano configuration. The analyses were done at relatively small angles ($0.5^\circ \leq 2\theta \leq 10^\circ$) to determine the degree of intercalation/exfoliation of clay from the clay interlayer spacing, d_{001} , by means of Bragg's law ($\lambda = 2d_{001} \sin \theta_{001}$). TEM observations were made on cryogenically ultra-microtomed thin sections using a high resolution TEM Hitachi H 9000 at 300 kV. FEGSEM observations were made at low voltage on surfaces of cryogenically fractured samples, after depositing a thin platinum layer on the surfaces by ion sputtering. Computer-assisted image analysis of carefully etched pre-polished specimens was also performed to obtain the surface particle density (number of particles per mm^2) at two different magnifications, 3000 $\times$ and 15,000 $\times$, which represent the surface particle density in the micron range (i.e., above 1 μm) and the sub-micron range (i.e., between 200 nm and 1 μm), respectively. A minimum count of 300 particles per sample was used.

2.3. Conventional tensile testing

Tensile testing was done at room temperature according to ASTM D638 using a computer-controlled mechanical tester with a clip-on gauge extensometer. The tests were done at a crosshead speed of 5 mm/min. Young's modulus, yield stress and strain at break are reported. A minimum of five tests was performed for each reported value. The standard deviation of the reported values for Young's modulus and stress is within 5%.

2.4. Essential work of fracture method

The EWF method consists of measuring the load–displacement curve of specimens containing a severe stress concentration zone designed to obtain a fully developed plastic zone in the fracture region. From this curve, it is possible to calculate the energy required to produce this plasticized fracture region, W_F , which can be expressed as a function of the EWF, W_e , and the non-EWF, W_p :

$$W_f = W_e + W_p = w_e \cdot l t + w_p \cdot \beta l^2 t \quad (1)$$

where w_e and w_p are the specific values for W_e and W_p , l and t are the ligament length and thickness of the fracture specimen, and β is a shape factor associated with the dimension of the plastic zone normal to the crack plane. Thus, by normalizing Eq. (1), the specific total work of fracture, w_t , is expressed as a linear function of l , the ligament length:

$$w_t = w_{\text{init}} + w_{\text{prop}} = w_{e,\text{init}} + (\beta w_p)_{\text{init}} \cdot l + w_{e,\text{prop}} + (\beta w_p)_{\text{prop}} \cdot l \quad (2)$$

from which the values of EWF for crack initiation and crack propagation, $w_{e,\text{init}}$ and $w_{e,\text{prop}}$, and the values of non-EWF for crack initiation and crack propagation, $(\beta w_p)_{\text{init}}$ and $(\beta w_p)_{\text{prop}}$, are obtained respectively by least-squares regression of $w_{t,\text{init}}$ vs. l and $w_{t,\text{prop}}$ vs. l data as the Y -axis intercept and the slope. The stress criterion, as described in the EWF test protocol [8], was applied to EWF data to ensure their validity. The mean value of the maximum stress of the DDENT specimens of each material was obtained and specimens for which the maximum stress was not within $\pm 10\%$ of the mean stress were rejected.

Fracture testing of the 1-mm thick plates was done at room temperature and a crosshead speed of 1 mm/min to obtain EWF measurements according to the ESIS protocol [8] using the mechanical tester described previously. A longitudinal video extensometer with a nominal gage length of 20 mm was used to measure the specimen deformation without touching the fracture test specimens. Deeply double edge-notched tension (DDENT) specimens with a width of 30 mm and an overall length of 80 mm were machined from the 1-mm thick sheets. Both notches in the specimens were carefully machined to ensure parallelism and symmetry. A very sharp notch was then produced by gently pressing a fresh razor blade into the notch root. The distance between the two notches, defined as the “free ligament length”, varied between 3 mm and 21 mm for each material tested with at least two specimens for each ligament length used. A minimum of 20 specimens per material was tested.

2.5. Fracture surface analysis

Fracture surface analysis on the DDENT was also performed to determine the mechanisms of failure and other specific characteristics of the materials tested. These fractographic observations were done using a HIT-ACHI S4700 FEGSEM, after depositing a platinum layer on the fracture surfaces by ion sputtering.

3. Results and discussion

3.1. Microstructure

Image analysis results of surface density in clay particles in the PNCs studied, along with examples of FEG-SEM observations, are shown in Fig. 1. This figure illustrates clearly the non-negligible presence of particles in both the micron and sub-micron ranges. It also shows that for 2 wt.% clay, the micron-range particle density progressively decreases as the sub-micron-range particle density increases. The use of LMW and IMW appears to lead to generally lower micron-range particle density than HMW.

XRD patterns of the PNCs studied (L-PNC1, I-PNC1 and H-PNC1) are shown in Fig. 2. Based on d_{001} measurements, this figure shows that good intercalation of clay particles was obtained. The highest average intercalation level of the PNCs based on Bragg's law was obtained for L-PNC, and the lowest for H-PNC. For I-PNC, the intercalation level obtained was between the previous two. It can also be observed that the clay intercalation peak varied in intensity and width for the different coupling agents. The narrowest and most intense was obtained for L-PNC, while I-PNC and H-PNC peaks are wider and less intense. This observation indicates that a wider range in clay interlayer spacing was obtained for I-PNC and H-PNC than for L-PNC. In other words, LMW was more effective in leading to a uniform intercalation level than IMW and HMW, although not exceptionally high intercalation levels were achieved (organo-modified clay already at 2.8–3.0 nm [12]), but part of the clay particles in I-PNCs and H-PNCs showed the same level of intercalation as those in L-PNCs.

TEM observations were also made to verify if exfoliation occurred and to qualitatively assess the level of intercalation of clay particles in the PNCs studied, as shown in Fig. 3. These observations reveal that a very

Fig. 1. Surface density measured at 3000 $\times$ magnification ($>1\text{ }\mu\text{m}$) plotted as a function of surface density measured at 15,000 $\times$ magnification (between 200 nm and 1 μm). Surface density at 3000 $\times$ in PP/clay is $44 \times 10^3\text{ mm}^{-2}$. Surface density at 15,000 $\times$ in PP/clay could not be obtained due to large particle size. SEM micrographs of PNC microstructure at 1000 $\times$ are shown as examples for three PNCs.

Fig. 2. XRD spectrum obtained for L-PNC1 (LMW), I-PNC1 (IMW) and H-PNC1 (HMW). Maximum clay interlayer spacing d_{001} is shown for each PNC.

fine dispersion of clay aggregate in the 100 nm–1 μm range was obtained. Complete exfoliation, i.e., complete separation of individual clay layers, could not be obtained irrespectively of the molecular weight of the coupling agent used. Most of the clay particles observed are multiple stacks of clay layers, although some particles correspond to single, double and triple stacks. Such clay dispersion was shown to yield very promising results in terms of mechanical properties [12], but it is not possible to quantitatively compare exfoliation levels obtained using LMW, IMW and HMW coupling agents from the observations shown in this study. Aggregate dispersion in PP/clay (without a coupling agent), not shown here, was considerably worse, with significantly larger clay aggregates, as observed previously [4].

Fig. 3. TEM observations at lower and higher magnification for (a) H-PNC, (b) I-PNC, and (c) L-PNC.

3.2. Conventional tensile properties

Young's modulus (E) and yield stress (S_y) are shown in Fig. 4 in terms of relative improvements with respect to PP properties ($E_{PP} = 1.49$ GPa and $S_{y,PP} = 26.9$ MPa). Elongation at break was above 500% for all materials tested. The results in Fig. 4 indicate that the fabricated PNCs have Young's modulus values that approximately rank with their yield stress values. They also indicate that improvements up to approximately 50% in Young's modulus and 25% in yield stress are obtained. These tensile results indicate that H-PNCs show more variations in Young's modulus improvement (between 0.30 and 0.43) than L-PNCs (between 0.41 and

Fig. 4. Relative Young's modulus (E) and yield stress (S_y) improvements for L-PNC (LMW), I-PNC (IMW) and H-PNC (HMW) with respect to PP values. The square symbol at lower left represents PP values. The straight line represents a linear least-square curve fit forced through PP values for indication purposes.

0.42) and I-PNCs (between 0.43 and 0.49), in agreement with their respective particle dispersion shown in Figs. 1 and 2. Improvements in mechanical results are in general higher in the case of I-PNCs, although fairly high yield stresses were obtained for H-PNCs.

To obtain a reference on the Young's modulus improvement levels that can be expected from such nanocomposites, the Halpin–Tsai micromechanical model is often used [13] with assumptions of perfectly aligned clay platelets in the tensile direction and aspect ratio defined as their length-to-thickness ratio. Using these assumptions in the Halpin–Tsai model, the Young's modulus improvement levels reported correspond to clay platelet aspect ratios of the order of 135, i.e., not far from perfectly exfoliated clay particles. Yield stress improvements, however, are lower than the theoretical improvements calculated from Cox's shear lag model [14] using an orientation factor representing partially oriented particles (orientation factor of 0.69 generally admitted for injection molding specimens), and correspond to lower clay particle aspect ratios of the order of 80, i.e., well intercalated, partially exfoliated clay particles in the 200–300 nm range in length. This observation supports the TEM observations presented in Fig. 3, where such high aspect ratio particles are observed. However, a more important part of the clay particles shown in Fig. 3 show a considerably lower aspect ratio, closer to the aspect ratio of 30 already reported [4]. It is not, however, possible to omit the effect of crystallinity and crystalline morphology, including orientation, on these property enhancements, which are not considered in the present paper. These effects are considered in another publication [15].

3.3. Fracture toughness results

Examples of the load–displacement curves from DDENT specimens are shown in Fig. 5 for PP, PP/clay, L-PNC, I-PNC and H-PNC. These curves exhibit the required self-similarity for EWF tests to be valid. They can be dissociated into two distinctive fracture regions. The first region corresponds to crack initiation and ends when a maximum is reached in the load–displacement curve. At this maximum, the crack starts to propagate, which defines the second region. The curves in Fig. 5 show that PP and PP/clay specimens exhibit a fairly brittle behavior, where most, and in the case of PP/clay, even all, of the strain energy is absorbed during crack initiation. In the case of L-PNCs, I-PNCs, and H-PNCs, well-developed crack initiation and crack propagation regions are observed on the load–displacement curves. However, the load–displacement curves in Fig. 5 suggest that final fracture and crack propagation regimes are not distinct. The specific EWF for crack propagation is thus not considered herein, following proposed energy-partitioning methods [10,11].

Fig. 5. Load–displacement curves of DDENT specimens with different ligaments indicated for (a) PP, (b) PP/clay, (c) L-PNC1, (d) I-PNC1, and (e) H-PNC1.

The specific work of fracture for the crack initiation–ligament length curves obtained is reported in Fig. 6. Values of $w_{e,init}$ and of $\beta w_{p,init}$ obtained respectively from the Y-axis intercept and the slope of a linear least-square regression calculated from Eq. (2) are reported in Table 2. Least-square regression squared correlation coefficients for PP/clay, L-PNC, I-PNC, and H-PNC were acceptable to good, varying from 0.81 to 0.93. PP showed a standard deviation of $w_{e,init}$ data of 0.09. The flat slope of the $w_{e,init}$ curve obtained for PP is caused by the difficulty to fully develop a plane stress condition in PP. However, in the present paper, this $w_{e,init}$ value for PP only serves as a reference and is not the object of this paper.

The results in Table 2 also indicate that $w_{e,init}$ varies considerably among the materials tested. Adding clay to PP without coupling agents led to a decrease in $w_{e,init}$ by more than 75%. Using coupling agents led to quite

Fig. 6. Specific work of fracture for crack initiation–ligaments length curves for EWF tests for (a) PP (closed square) and PP/clay (open square), (b) L-PNC, (c) I-PNC and (d) H-PNC. For L-PNC, I-PNC and H-PNC, PNC1 is represented by triangle symbol and PNC2 by square symbol. Dotted line represents a least-square curve fit according to Eq. (2) to determine values of EWF, $w_{e,init}$, and non-EWF, $(\beta w_p)_{init}$.

Table 2

EWF test results (r^2 : squared correlation coefficient)

Material	$w_{e,init}$ (kJ/m²)	$(\beta w_p)_{init}$ (MJ/m³)	r^2
PP	7.8	0.0	–
PP/clay	1.9	0.4	0.82
L-PNC1	7.4	0.4	0.81
L-PNC2	7.2	0.4	0.87
I-PNC1	9.3	0.3	0.82
I-PNC2	9.2	0.7	0.93
H-PNC1	5.7	0.4	0.91
H-PNC2	5.9	0.4	0.88

different $w_{e,init}$ values, depending on the type of coupling agent used. H-PNCs showed $w_{e,init}$ values approximately 25% below those of PP. L-PNCs showed $w_{e,init}$ values within 10% of those of PP, while I-PNCs showed

Fig. 7. EWF ($w_{e,init}$) values plotted against surface density at 3000 $\times$ magnification. H-PNCs, I-PNCs, and L-PNCs are represented by square, round, and triangle symbols (solid), and PP/clay by open square symbol. Drawn line indicates trend only.

$w_{e,init}$ values improved by 20% with respect to PP values. Although promising, such improved $w_{e,init}$ values are still below requirements for most automotive exterior applications [16]. While the formulation had a substantial effect on the $w_{e,init}$ term, it does not appear to significantly affect the plastic dissipation term, $(\beta w_p)_{init}$; values obtained varied between 0.3 and 0.4 MJ/m³, with the exception of I-PNC2, which showed values of 0.7 MJ/m³.

Since the presence of clay aggregates in PNCs is expected to play a role in their fracture behavior, $w_{e,init}$ results were plotted against particle surface density (mm⁻²) as presented in Fig. 1. This $w_{e,init}$ –surface density curve is shown in Fig. 7, using the larger particle population characterized (at 3000 $\times$), representing micron-sized particles. Despite substantial scatter in the data, arising from image analysis, a clear trend can be observed: as surface density in larger size particles increased, $w_{e,init}$ decreased. This trend is in agreement with the expected effect of large particles acting as void initiating defects in PP. No such trend could be identified when plotting $w_{e,init}$ as a function of the sub-micron particle population characterized (at 15,000 $\times$). It thus appears that the fracture behavior of PNCs is determined by more than one effect. On one hand, mechanical properties, in particular fracture resistance, are increased by reinforcement effects that are related to exfoliated/intercalated nanoparticles characterized in Figs. 1–3, and reported in Fig. 4 by tensile properties and Fig. 6 by work of fracture curves. These reinforcement effects are in agreement with expected reinforcement from nanoparticles using micro-mechanical calculations. The results show also that sub-micron particles (200 nm–1 μ m) are not the ones controlling these reinforcement effects, since no correlation could be established between sub-micron particle surface density and $w_{e,init}$. On the other hand, the level of fracture resistance improvement expected from nanoparticles appears to be limited, or obscured, by the presence of larger clay aggregates remaining in the fabricated PNCs, as shown in Fig. 7. Thus, the ability to obtain a uniform distribution of sub-micron particles or even nanoparticles free of any larger size aggregates represents the limitation to fracture behavior enhancement. I-PNCs containing an intermediate M_w coupling agent had the best clay particle dispersion and showed the best $w_{e,init}$ results.

3.4. Fractographic observations

Fractographic observations were made to understand the influence of PNC nano/microstructure on the fracture behavior, especially the mechanisms that lead to their fracture. For PP/clay, fracture surfaces feature voids separated by fairly short ligaments (Fig. 8a). These voids were formed at large clay aggregates (Fig. 8b) and grew in size under the imposed deformation until they coalesced with neighboring voids. This coalescence

Fig. 8. Fractographic observations of PP/clay at (a) low (200 $\times$), (b) intermediate (4000 $\times$), and (c) high (20,000 $\times$) magnification.

left ligaments of unbroken matrix that bridged the crack process zone and eventually failed. Higher magnification observation of PP/clay fracture surface shows that clay aggregates were large, above 1 μm in size, and that very low particle–matrix adhesion prevailed (Fig. 8c). The presence of such large defects (stress concentrators) poorly coupled to a low toughness matrix explains the brittle behavior obtained for this material. L-PNCs specimens (Fig. 9) failed essentially in a similar fashion, but fracture surfaces feature fewer, larger voids with considerably elongated ligaments. Clay particles were also smaller, and appeared attached to deformed matrix, either in ligaments or in voids. Similar fewer, larger voids with considerably elongated ligaments were observed on the fracture surfaces of I-PNCs and H-PNCs. The matrix deformed in small elongated fibrils, between which important microvoid formation was observed. Such microvoids are shown for L-PNCs, I-PNCs, and H-PNCs (Figs. 9b, 10 and 11). At least in the case of I-PNCs (Fig. 10), for which it

Fig. 9. Fractographic observations of L-PNC1 at (a) low (200 $\times$) and (b) high (15,000 $\times$) magnification. Arrows indicate clay particles.

Fig. 10. Fractographic observations of I-PNC1 at high (20,000 $\times$) magnification. Arrows indicate clay particles.

Fig. 11. Fractographic observations of H-PNC1 at high (25,000 $\times$) magnification. Arrows indicate clay particles.

was very clear, very small high aspect particles remained attached to the elongated fibrils observed. Similar observations could at times be made for H-PNC (Fig. 11), although to a lesser extent.

Fractographic features identified in PNCs here correspond to key fracture mechanisms well known to result in high fracture energy (total work of fracture), ductility (non-EWF) and fracture toughness (EWF) in filled polymers. Fracture surfaces of PNCs reveal the presence of very small, evenly dispersed voids in the matrix and of a high number of very long fibrils between these voids. These observations indicate that fracture occurs by void initiation at very small clay particles ($\ll 1 \mu\text{m}$) that are well bonded to the matrix. Due to their volume (or surface) density, size and interfacial adhesion, initiation requires considerable fracture energy and is postponed at higher stresses, resulting in higher fracture toughness. Once voids are initiated, their growth and coalescence is controlled by the stability of the fibrils extension and the resistance of the particle–matrix interface.

Fracture surfaces of PP/clay are quite different in that they only show significantly larger particles that are poorly bonded to the matrix. In this case, void initiation occurs at significantly lower stresses (stress concentrations related to particles are proportional to their nominal surface in the loading plane) and void growth and coalescence occur rapidly due to the lack of reinforcement of the matrix, PP itself not being very tough, leading to a close to brittle behavior.

Observations revealed that at least in the highest fracture toughness PNCs, sub-micron high aspect particles were observed attached to highly elongated fibrils. Fibrils in this case could be described as oriented (or elongated) polymer strands reinforced by high aspect ratio particles, which would lead to an significant reinforcement effect. Such a behavior would then require more energy to failure and explain at least part of the improved fracture toughness, attributed to the second part of the load–displacement curves of DDENT specimens. This orientation of nanoparticles during solid-state deformation leading to a reinforcement effect has been reported in cellular materials (e.g., foams) in which the cell walls contain oriented nanoclays [17–19].

4. Conclusions

PNCs were produced by TSE melt compounding of PP with equal amounts (2 wt.%) of commercial organo-modified montmorillonite clay and MAgPP with varying molecular weight. SEM, XRD, and TEM analyses showed that good clay intercalation levels (between 3.0 and 3.5 nm) and partial clay exfoliation were obtained, but that the surface density in clay particles at the micron scale and sub-micron scale was not negligible. The molecular weight of MAgPP used as a coupling agent for clays had an effect on the quality of the clay particle dispersion. Intermediate and low M_w generally led to better clay dispersion (i.e., fewer larger clay particles), with the lowest micron scale surface density observed for intermediate M_w . High M_w led to higher micron scale and lower sub-micron scale surface densities in clay particles.

Tensile testing showed that coupled PNCs had significant improvements in Young's modulus (50%) and in yield stress (25%). A correlation could be established between the quality of clay dispersion and the tensile properties improvements. Moreover, tensile properties improvements were only slightly lower than those predicted using micro-mechanical models (e.g., Halpin–Tsai or Cox's shear lag) with very high aspect ratios (≈ 135) corresponding to nanoclay platelets dispersion. These mechanical reinforcements observed are thus related to nano-scale effects (i.e., extremely high density in high aspect ratio, well-coupled nanoparticles) but probably also to other effects such as crystallinity and crystalline morphology, orientation, etc.

Fracture toughness was characterized by means of EWF for crack initiation ($w_{e,init}$). PNCs curves showed well-defined crack initiation and propagation regions, whereas PP and PP/clay, more brittle, showed either very minor crack propagation regions or none. Again, the quality in clay dispersion could be correlated to $w_{e,init}$ results; PNCs with lower micron scale clay particles proved to be those with highest $w_{e,init}$. Such a correlation, however, could not be established between $w_{e,init}$ and surface density in sub-micron scale clay particles. This probably indicates that the reinforcement or toughening effects observed here are indeed related to the nanoscale particles, as concluded from tensile results analysis.

Fractographic observations clearly illustrated the role of larger size clay particles as void initiation sites. Following their initiation, these voids grew in size under the imposed deformation until they coalesced with neighboring voids. This coalescence left ligaments of unbroken matrix that bridged the crack process zone and eventually failed. At least in PNCs showing significant ligament formation, very small high aspect particles attached to these ligaments and oriented along their length were observed. In addition to improvements in toughness arising from generally smaller clay particles initiating voids at higher stresses, this observation suggests that improvements in toughness could also be attributed to matrix reinforcement through the presence of oriented, high aspect ratio nanoparticles in the ligaments.

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