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IMI 2007-116724-G
CNRC 49637

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Polymeric Nanocomposites: compounding and performance

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Melt compounding of Polymeric Nanocomposites

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ABSTRACT

Polymeric nanocomposites (PNC) are binary mixtures of strongly interacting, inorganic platelets dispersed in a polymeric matrix. For full exfoliation, the thermodynamic miscibility is required. There are three basic methods of organically-modified clay dispersion that might result in PNC: 1) in polymer solution (followed by solvent removal), 2) in a monomer (followed by polymerization), and 3) in molten polymer (compounding). Most commercial PNC are produced by the second method, but it is the third one that has the greatest promise for the plastics industry. Similarly as during the manufacture of polymer blends, the layered silicates must be compatibilized by intercalation with organic salts and/or addition of functionalized macromolecules. Compounding affects the kinetics of dispersion process, but rarely the miscibility. Melt compounding is carried out either in a single-screw (SSE) or a twin-screw extruder (TSE). Furthermore, an extensional flow mixer (EFM) might be attached to an extruder. Two versions of EFM were evaluated: (1) designed for polymer homogenization and blending, and (2) designed for dispersing nano-particles. In this review, the dispersion of organoclay in polystyrene (PS), polyamide-6 (PA-6) or in polypropylene (PP) is discussed. The PNC based on PS or PA-6 contained two components (polymer and organoclay), whereas those based on PP in addition had a compatibilizer mixture of two maleated polypropylenes. Better dispersion was found compounding PNC's in a SSE + EFM than in TSE with or without EFM. The mechanical performance (tensile, flexural and impact) was examined.

Keywords: *nanocomposite, clay, extrusion, compounding, extensional flow mixer*

1 Introduction

Polymeric nanocomposites (PNC) are used as either functional or structural materials. The functional ones are used in applications where specific functionality is required, *e.g.*, electrical conductivity, electronic semi-conductivity, magnetic properties, bio-compatibility. For example, conductive PNC have been used for capacitors, rechargeable battery materials, or in electrochromic windows. However, in this paper the structural PNC are of interest. For these large volume systems the mechanical behavior is of main concern (followed by gas/vapor barrier properties, flammability, *etc.*). For these applications the only nano-sized particles of industrial interest are layered minerals, mainly montmorillonite (MMT) and hectorite (HT).

Since the beginning, the PNC have been produced by the resin manufacturers by dispersing clay in monomer and then polymerizing it [^{1, 2, 3}]. Development of reliable melt compounding technology will provide compounders and fabricators means for the manufacture of compositions with required properties, where and when they are needed. The melt compounding is flexible, rapid, environment friendly, and inexpensive. Development of this technology will greatly accelerate PNC acceptance by the plastics industry and its market expansion.

The global market for PNC exceeds \$200 million, to reach 550 kton/y by 2009 [^{4, 5}]. The application ranges from the transport industry (*e.g.*, GM, Mitsubishi, Toyota), to packaging, appliances, building & construction, electrical & electronic, lawn & garden, power tools, sport equipment, *etc.* There is a rapid growth of PNC utilization for coating (*e.g.*, scratch resistant), surface finish, barrier properties, and controlled release of various chemicals.

The melt compounding is carried out in compounding extruders or internal mixers; both of which employ the shear field to generate the dispersive and distributive mixing. However, it has been recognized that the extensional (irrotational) flow field is more energy-efficient as it generates better mixing without the temperature increase [^{6, 7, 8}]. Consequently, an extensional flow mixer (EFM) and its dynamic version, DEFM were developed for polymer homogenization and blending [^{9, 10}]. Unexpectedly, it has been found that EFM attached to a single-screw extruder (SSE) better dispersed organoclays in thermoplastic matrices (PET, PA-6, PP, and PS) than a twin-screw extruder (TSE) [^{11, 12, 13}]. For example, the tensile modulus (E), strength (σ)

and impact strength (*NIRT*) of PET-based specimens prepared using TSE + EFM were up to 70% higher than when TSE was used alone. Encouraged by these findings a new mixer (EFM-N) for dispersion of organoclays during PNC compounding was designed by modifying the EFM-3 flow channels geometry.

This review comprises two main parts: fundamentals of PNC that affect melt compounding, and an outline of melt compounding of several PNC systems. The results of compounding are evaluated considering the clay dispersion and mechanical performance.

2 Fundamentals

2.1 Thermodynamics

Owing to the nano-size of clay platelets (more than 40% atoms are on the surface), PNC must be treated as a molecular mixture of two species. Clay exfoliation depends on the system miscibility and kinetics – compounding controls only the latter.

Molecular mechanics (MM) has been used to investigate diverse properties of polymeric systems controlled by the thermodynamics and kinetics [14]. The MM methods adopt diverse chain models to represent structures and interactions. The computations are expensive and time consuming, thus often simplified ones are used, *e.g.*, the lattice models based on statistical mechanics. Here, the polymer chains are represented by random walks on numerical lattices, and similarly clay platelets are treated as large molecules [15]. Lattice theories are mean-field type as they do not consider detailed molecular structure. The lattice-based, self-consistent mean field (SCF) approach [16] has been used by Balazs and co-workers [17, 18, 19, 20, 21]. The authors modeled PNC as two infinite parallel clay platelets immersed in a bath of molten polymer. Kim *et al.* extended this two-component 1D model to four-component PNC (clay, intercalant, polymer, and compatibilizer) in 2D; the aim was to simulate the clay dispersion in PP-based PNC [22]. The simulation showed that intercalation and exfoliation is expected only within limited ranges of independent variables. The presence of bare clays on the one hand hinders the dispersion, but on the other provides opportunity for interactions with compatibilizer polar groups. The simulation identified the most influential factors that control free energy of the system.

2.2 Molecular adsorption

The high surface energy of crystalline solids causes adsorption and immobilization of molecules, *e.g.*, gases and vapors from air, macromolecules from solutions or melts, etc. [23, 24]. The experiments and mathematical models suggest that the reduced chain mobility is a general phenomenon [25]. The thickness of the solidified layer on each side of clay platelet surface is 4 to 6 nm, what multiplies the solid content by a factor of 9 to 13. Furthermore, the macromolecular mobility exponentially increases with the distance from clay surface, reaching its bulk mobility at a distance of 100 to 120 nm. Evidently, these layers of low mobility hamper clay dispersion. Judging by the reduction of polymer free volume caused by the addition of clay, the adsorption is equivalent to lowering the compounding temperature by *ca.* 50°C [1]. Compounding at higher temperatures would be a solution to the immobilization problem. However, due to poor thermal stability of the ammonium intercalants, at present this route is rarely practical. Thus, the only strategy is to develop systems with strong thermodynamic interactions.

2.3 Thermal instability of organoclays

The ammonium-ion intercalated organoclays degrade at $T \geq 180^\circ\text{C}$ by the Hofmann elimination mechanism [26] leaving the clay surface bare, what might cause re-aggregation of clay platelets and loss of performance:

The reaction by-products are volatile amine and a double bond terminated the longest paraffinic substituent, R. Evidently, the vinyl terminal group might oxidize forming peroxide capable to initiate free radical chain scission of the matrix polymer. Replacing the aliphatic groups by aromatic or branched substituents, using secondary or tertiary amines, might improve stability. Replacing ammonium by phosphonium ions or using organo-metallic complexes is also beneficial [2]. However, currently the thermal degradation of commercial, ammonium intercalated organoclay is a painful reality.

2.4 Maximum packing volume fraction

The monodispersed hard spheres suspensions change from liquid-like to solid-like when the particles volume fraction exceeds the critical value $\phi_c \approx 0.62$. When hard spheres are replaced by anisometric particles, the properties also change at ϕ_c , but this concentration ought to be calculated from the volume the particle needs for the free rotation. Assuming monodispersed, circular disks with diameter d and thickness t (aspect ratio: $p = d/t$) the ratio of the encompassed to actual volume is: $V_{enc}/V = 2p/3$. Most commercial clays have $p \approx 280$, thus $\phi_c \approx 0.0033$, or *ca.* 1-wt%. In other words, exfoliation is possible only for $\phi \leq \phi_c$. At higher clay contents the geometry forces platelets to form local stacks with progressively (with ϕ) reduced interlayer spacing.

It is noteworthy that the above arguments are valid for PNC with liquid or glassy matrix. When the matrix is semi-crystalline (*e.g.*, PP) the clay is expected to be expelled from the crystal phase during crystallization. Empirically, the following linear relation was applied [27]:

$$d_{001} = d_{001}^0 - a_1 C_{clay} - a_2 X \quad (1)$$

Eq. 1 was obeyed for PP-based PNC with $d_{001}^0 = 10.5 \pm 0.6$, $a_1 = 0.39 \pm 0.05$, $a_2 = 0.11 \pm 0.01$, and the correlation coefficient $r = 0.999$. Thus, infinitely diluted, amorphous PP-based PNC would be exfoliated ($d_{001} = 10.5$ nm), but as the clay concentration (C_{clay}) and the crystalline content (X) increase, the interlayer spacing is reduced to $d_{001} \approx 3$ to 3.5 nm.

2.5 Melt compounding

Melt compounding takes place in an extruder, internal mixer, or a similar device. Industrially, PNC is considered exfoliated when ≥ 80 wt% of clay platelets are uniformly dispersed in the matrix. Two compounding methods have been employed [2]:

- (1) A single-step process (SP) that leads to the final PNC composition. Here, the matrix polymer is melted, an organoclay (and a compatibilizer if needed) is added, and then mixed under blanket of N_2 (alternatively, the polymer may be mixed with a compatibilizer and then organoclay added).
- (2) A two-step process where concentrated master batch (MB) is prepared first, and then diluted to the required concentration.

The commercial organoclay is a powder with aggregated particles of *ca.* 12 μm diameter. Compounding must break these aggregates and disperse clay platelets, by rupture and “peeling” mechanisms [28]. After the aggregates are broken into clay stacks, the macromolecules should diffuse into the interlamellar galleries and thus facilitate peeling. The diffusion takes place when the polymer and organoclay are miscible, and the interlamellar gap is sufficiently large, e.g., $d_{001} > 1.35 \text{ nm}$. Evidently, the process must lead to the reduction of the system free energy of mixing, ΔG_m . While the thermodynamics determines the potential for organoclays dispersion, the kinetics decides how far the process might progress during the residence time in the compounding device. There are indications that the diffusion step is controlled by strain not stress [27, 29].

During the melt compounding of multiphase polymeric systems, the mixers employing shear cause the flow elements (e.g., organoclay aggregates) to be repetitively stretched and compressed – the theory and experiments have shown that in the shear field the dispersion is feasible only when the ratio of the dispersed phase viscosity to that of matrix is low, $\lambda < 4$ [30, 31]. Evidently in the case of polymer/organoclay systems λ is large, and shear dispersion is ineffective. By contrast, such a limit does not exist for mixing in the elongational flow field.

The fundamental understanding of micro-rheology in laminar flow led to designing EFM for polymer homogenization or blending [9]. The device employs the convergent-divergent (C-D) flow that stretches the flow elements in the flow direction and then in transverse direction. The EFM-3 was commercialized for the throughputs of $\leq 2 \text{ tons/h}$ [32]. It has a sturdy design with dimensions that are virtually independent of internal pressure. A schematic of the motionless EFM is presented in Fig. 1. Its dynamic version, the dynamic extensional flow mixer (DEFM), is in the form of conical torpedo, normally attached to the SSE barrel and screw [8]. Depending on the need, its dispersive and distributive elements might be added.

Fig. 1. Schematic of EFM; the heart of the device is the converging/diverging (C-D) flow zone with the gap, h , between the upper and lower plates.

Since the mechanism of drops dispersion is different than that of clay aggregates, there was a need for redesigning the EFM for PNC compounding. First, a screw-version of DEFM was designed, built, and tested for the PS-based PNC [33]. Next, the C-D profile geometry of the most effective DEFM design was adopted in the new EFM-N [34]. This review summarizes the compounding experience in NRCC/IMI laboratories using SSE, or TSE, with and without EFM-3 or EFM-N. The PNC's with PS, PA-6 and PP matrices will be discussed and general conclusions drawn. For details the reader might want to consult the original publications.

3 Experimental

3.1 Materials

A series of PS [35,36,37], PA-6 [34,38], and PP-based [34,38] PNC compositions was prepared, by SP or MB method, with variable organoclay content. For PP-based PNC a mixture of two PP-MA was used as compatibilizer. The materials characteristics are listed in Table 1.

Table 1. Material characteristics¹.

Material	Trade name	M_w ² (kg/mol)	Density (g/mL)	T_m (°C)	MAH (wt%)	Supplier	Ref.
PS	PS-1301	270		-	-	NOVA Chemicals	35, 36, 37
PA-6	Ube-PA1015B	21.7	1.14	216	--	Ube Industries	34, 38
PP	PROFAX-PDC1274	250	0.902	161	--	Basell Polyolefins	34, 38
PP-MA1	Epolene-3015	47	0.91	162	1.31	Eastman Chemicals	34, 38
PP-MA2	Polybond 3150	330	0.91	164	0.5	Crompton	34, 38
C10A	Cloisite® 10A	--	--	--	--	South. Clay Prod.	35, 36, 37
C15A	Cloisite® 15A	--	--	--	--	South. Clay Prod.	34, 38

Notes: ¹ Abbreviation list is provided in the Appendix. ² Polymers with other molecular weights than these listed in the Table have also been investigated – see the cited references.

3.2 Equipment

The PNC's were prepared using a TSE, TSE + gear pump (GP), TSE + GP + EFM, or a SSE with or without EFM. For comparison, EFM-3 and EFM-N were used with several C-D gap settings, h . It was observed that for most systems the MB procedure yields better results than SP [39], thus the MB process has been employed. Owing to the large volume of data and limited journal space, here only the main findings are discussed – for details please consult the original references.

TSE was a Leistritz-34mm CORI, L/D = 40, with screw speed $N = 200$ rpm, and throughput $Q = 5$ and 10 kg/h. Low and high shear screw configurations were used [33]. Compounding was done under dry N₂ at the temperatures of $T = 200^\circ\text{C}$ for PS, $T = 180$ and 200°C for PP, and 240°C for PA-6 systems. GP Model EH 45/28 was from Maag Pump System. SSE was a Flag 63.5 mm machine with L/D = 24, and a two-stage Dry mixing screw. The EFM-3 and EFM-N were used with the C-D gap settings ranging from $h = 5$ to 2000 μm . To be able to place the data for SSE, TSE, and TSE + GP on graphs illustrating the effects of the EFM gap changes, the value of $h = 4$ mm was arbitrarily assigned to extruder + strand die, and $h = 3$ mm to TSE + GP.

In-line measurements of the residence time (t_R) and its distribution (RTD) during extrusion compounding were conducted at ultrasonic frequency of 5 MHz with *ca.* 5 g of CaCO₃ as a tracer [40]. The results for TSE and SSE at $Q = 5$ kg/h are listed in Table 2.

Table 2. The mean residence time in TSE and SSE at $Q = 5$ kg/h.

Twin-screw extruder (TSE)		Single-screw extruder (SSE)	
System	t_R (s)	System	t_R (s)
TSE	139	SSE	1163
TSE + GP	236	--	--
TSE + GP +EFM open	320	SSE +EFM open	1147
TSE + GP +EFM closed	368	SSE +EFM closed	1108

3.3 Compounding

Prior to processing all the ingredients were dried in a commercial drying tower. First, the relative merits of the two processing methods, SP and MB, were evaluated, and on this basis the latter was adopted. For SP either SSE or TSE extruder could be used, but for MB the first compounding was carried out in TSE with a screw side-feeder, and then the dilutions to 2 or 4-wt% in either SSE or TSE, with or without EFM. When EFM was used, the pressure between the C-D plates linearly decreased with the logarithm of the C-D gap, h (μm) [30]. According to the X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEGSEM), transmission electron microscopy (TEM), and mechanical tests, the MB method led to better (than SP) performance. Even for PP-based PNC, in spite of greater matrix degradation, an improvement over SP was registered.

3.4 Characterization

The mechanical tests were carried out according to ASTM. The PNC specimens containing 0, 2, and 4-wt% organoclay were injection-molded in Engel 150T into end-gated ASTM mold. For the determination of clay dispersion TEM-specimens were prepared from the middle, central part of the dogbone.

The XRD measurements were carried out using a Brker D8 Discover with $\text{CuK}\alpha$ radiation. From the spectra three measures of the degree of dispersion were calculated: (1) the interlayer spacing, d_{001} , (2) the number of platelets per stack, N , and (3) the amount of clay platelets absent in stacks, related to the degree of exfoliation, Ex [2, 35]. The TEM observations at high resolution (HRTEM) were carried out using Hitachi H9000, while FEGSEM using Hitachi S4700. The

specimens were prepared by shaving *ca.* 70 nm thick sections from the dogbones at room temperature using a Leica Ultracut FC microtome with diamond knife. To detect large aggregates, some specimens for FEGSEM were fractured, while others were polished and chemically treated.

3.5 Mechanical tests

Prior to testing, the specimens were dried under vacuum. The tensile and flexural tests (ASTM D638 and D790, respectively) were carried out using an Instron 5500R and 1125 testers at the crosshead speed of 5 and 15.7 mm/min, respectively. The notched Izod impact tests at room temperature (*NIRT*) were performed using an impact tester Instron 8200 (ASTM D256). The values reported here are averages of at least ten tests for each sample.

4 Results

4.1 Clay dispersion in PS matrix

For PNC with PS as the matrix, XRD consistently showed the presence of two peaks, the 1st corresponding to the interlayer spacing of about $d_{001} \approx 4.5$ nm, and the 2nd of about $d_{001} \approx 1.7$ nm [34-36]. The peaks position depended on the residence time; hence processing line and throughput (Fig. 2), clay content (Fig. 3), and (not shown) compounding conditions. The 1st peak represents the intercalated organoclay stacks on the way to exfoliation, whereas the 2nd one the progressively collapsing interlayer spacing down to *ca.* 1.35 nm. The results are independent of PS molecular weight, $M_w = 230$ to 310 kg/mol. The FT-IR documented the thermal degradation of onium compounds as described by Hofmann. The process resulted in breakdown of C10A into benzyl dimethyl amine and a long-chain olefin that underwent oxidation, peroxide formation, and caused PS chain scission [32]. Degradation of organoclays has been reported for $T \geq 180$ °C [41, 42, 43]. The interlayer spacing of the 1st peak decreased with organoclay content, w , and because of the geometric crowding it reached a plateau for $w \approx 5$ wt% [2]. Thus, the increase in Fig. 3 for $w \approx 11$ -wt% was unexpected – it may indicate improved dispersion when compounding in highly viscous medium.

Fig. 2. Interlayer spacing in PS/C10A nanocomposites showing the residence time dependence for the 1st and the 2nd peak. Data ref. [35,37].

Fig. 3. Interlayer spacing in PS/C10A vs. organoclay concentration for the 1st and the 2nd peak (*n.b.*, $t_R \approx 200$ s; d_{001} of the 2nd peak was shifted up by 1 nm). Data ref. [].

TEM micrographs confirmed that the dispersive mixing was inadequate (few large agglomerates remained), but distributive mixing was satisfactory. In spite of immiscibility of PS with C10A, the PS macromolecules were able to diffuse into the intergallery space, and interact with the exposed by degradation clay surface, forming low mobility solidified layers.

Table 3. Summary of the XRD scans for PNC's based on PA-6 [].

C15A (wt%)	Specimen (compounder)	d_{001} (nm)	Platelets/stack, N (-)	Exfoliation Ex (%)
100	Cloisite® 15A	3.21	3.34	--
4	Master-batch (MB)	3.87	3.35	--
2	TSE	4.44	2.79	52.7
2	TSE+GP	4.42	2.89	64.7
2	TSE+GP+EFM-3; $h=5$ μ m	4.39	2.78	83.3
2	SSE + EFM-3; $h=30$ μ m	3.65	3.14	89.9
2	SSE + EFM-N; $h=30$ μ m	4.65	2.15	97.1
2	UBE1015C2	5.33	2.15	80.7

Notes: The listed values are averages of four tests. The error of measurements for d_{001} is ± 0.01 , for the number of pellets per stack is ± 0.22 , and for the degree of exfoliation is $\pm 3.5\%$.

Table 4. XRD data for PP-based PNC containing X-wt% C15A and 2X-wt% of compatibilizers.

C15A (X, wt%)	Specimen (compounder)	Interlayer spacing, d_{001} (nm)		Platelets/stack, N (-)	Excess Exfoliation, ΔEx (%)
		1st peak	2nd peak		
100	Cloisite® 15A	3.21	1.95/1.22	3.34	--
10	Master-batch	3.52	1.30	2.59	--
4	TSE+GP+EFM-3; $h = 63.5$ nm	3.17	1.35	2.83	18.1
2	TSE	3.57	1.35	2.59	0
2	TSE+GP	3.47	1.34	2.74	2.0
2	TSE+GP+EFM-3; $h = 15$ nm	2.95	1.34	2.79	28.9
2	SSE + EFM-3; $h = 15$ nm	3.32	1.35	3.10	27.1
2	SSE + EFM-N; $h = 15$ nm	3.09	1.35	3.00	28.7

Notes: The listed values are averages of four. The error of measurements for d_{001} is ± 0.03 nm, for the number of pellets per stack is ± 0.04 , and for the exfoliation excess is $\pm 1.2\%$.

4.2 Clay dispersion in PA-6 matrix

Table 3 summarizes XRD results for PA-6-based PNC compounded in TSE or SSE (the diffractograms are shown in Figs. 5 and 6 of ref. [1]). Judging by the featureless diffractograms, the SSE + EFM-N produced the highest degree of clay dispersion; exfoliation was confirmed by HRTEM.

4.3 Clay dispersion in PP matrix

The XRD measures of clay dispersion in PP + PP-MA matrix are summarized in Table 4, and the effect of the EFM gap is illustrated in Figs. 4 and 5. In these Figures, the data for extruders without EFM, are the gap for extruder with strand die as $h = 4$ mm (3 mm for TSE + GP). Similarly as it was the case for PS, here also the organoclay shows two peaks, 1st $d_{001} = 3.0$ to 3.6 nm, and the 2nd $d_{001} \approx 1.3$ nm. Two measures of C15A dispersion are displayed: in Fig. 4 the interlayer spacing, d_{001} , and in Fig. 5 the additional degree of exfoliation engendered by EFM, ΔEx , over what have been computed for PNC compounded in TSE or SSE without EFM [1].

As shown in Fig. 5, ΔEx systematically increases as the C-D gap decreases, *i.e.*, addition of EFM to the extrusion line reduces intensity of the X-ray coherent scattering. The effect is particularly evident for the TSE. Of the two extensional flow mixers attached to SSE the new EFM-N performs marginally better.

Fig. 4. EFM gap influence on C15A interlayer spacing in PP + PP-MA matrix, for TSE + GP + EFM, SSE + EFM-3, and SSE + EFM-N at $Q = 5$ kg/h. Data from ref [1].

Fig. 5. EFM gap effect on C15A exfoliation in PP + PP-MA matrix, for TSE + GP + EFM, SSE + EFM-3, and SSE + EFM-N at $Q = 5$ kg/h. Data from ref [1].

The XRD results were confirmed by FEGSEM and HRTEM. The former showed that in PNC prepared using EFM-N (with gap $h \leq 63.5\mu\text{m}$) C15A stacks were uniformly dispersed (absence of aggregates). The HRTEM micrographs indicated that compounding in SSE + EFM-N resulted in better dispersion than that in TSE + GP + EFM.

4.4 Mechanical properties of PS based PNC

The tensile modulus, E , was found to be independent of PS molecular weight, and linearly increasing with organoclay content [34-36]. The relative modulus might be written as [2]:

$$E_R = E/E_m = 1 + aw \quad (2)$$

where E_m is the matrix modulus, $a = a(p)$ is a parameter, and w is the organoclay content in wt%. As displayed in Fig. 6, compounding at higher temperature was beneficial. However, the slopes of Eq. 2 correspond to low aspect ratio, $p \approx 20$, suggesting stacks of about 5 clay platelets, in agreement with the XRD estimate [1]. Thus, addition of organoclay is relatively inefficient for stiffening PS, while the notched Izod impact strength ($NIRT$) is reduced (*e.g.*, from 12 to 9 J/m). It is noteworthy that within the full range of the explored variables $NIRT$ linearly correlate with the tensile strength, σ [1]. Fig. 7 shows that toughness (G ; computed from tensile data) parallels

the *NIRT* dependence, indicating that there is a simple linear relation between *NIRT* and *G*, thus apparently these properties depend on similar mechanisms.

Fig. 6. Tensile modulus of PS-based PNC vs. clay content at $T = 180$ and 200°C .

Fig. 7. *NIRT* and toughness of PS-based PNC vs. clay content

Table 5. Mechanical properties of PA-6 based PNC.

PNC samples	Tensile			Flexural		<i>NIRT</i> (J/m)
	<i>E</i> (GPa)	σ (MPa)	ϵ_b (%)	<i>E_F</i> (GPa)	σ_F (MPa)	
Masterbatch; 4-wt% C15A	3.58	78	59	3.40	135	28
TSE; 2-wt%C15A	3.37	80	82	3.47	152	24
TSE + GP; 2-wt%C15A	3.37	82	163	3.46	152	21
TSE + GP + EFM-3; 2-wt%C15A; $h = 5 \mu\text{m}$	3.32	82	145	3.61	155	25
SSE + EFM-3; 2-wt%C15A; $h = 30 \mu\text{m}$	3.73	91	123	3.61	151	29
SSE + EFM-N; 2-wt%C15A; $h = 30 \mu\text{m}$	3.77	90	93	3.62	151	26
PA1015C2 from Ube	3.80	94	94	3.92	165	24

Note: The experimental error for the tensile modulus (*E*), strength (σ), and elongation at break (ϵ_b) is ± 2 , 4, and 5%, respectively; that for the impact strength (*NIRT*) $\pm 12\%$.

Table 6. Mechanical properties of PP based PNC.

PNC samples	Tensile			Flexural		NIRT (J/m)
	E (GPa)	σ (MPa)	ϵ_b (%)	E_F (GPa)	σ_F (MPa)	
Masterbatch; 10-wt% C15A	2.94	32	2.34	56	15	15
TSE + GP + EFM-3; 4-wt%C15A; $h = 63.5 \mu\text{m}$	2.16	33	1.82	57	31	31
TSE; 2-wt%C15A	2.09	33	1.90	60	19	19
TSE + GP; 2-wt%C15A	2.15	33	1.84	59	23	23
TSE + GP + EFM-3; 2-wt%C15A; $h = 15 \mu\text{m}$	2.07	34	1.92	61	33	33
SSE + EFM-3; 2-wt%C15A; $h = 15 \mu\text{m}$	2.09	35	2.07	59	35	35
SSE + EFM-N; 2-wt%C15A; $h = 15 \mu\text{m}$	2.08	36	2.11	59	34	34

Note: The experimental error for the tensile modulus (E), and strength (σ) is ± 4 , and 5%, respectively; that for the impact strength ($NIRT$) $\pm 12\%$.

4.5 Mechanical properties of PA-6 based PNC

Prior to testing, the injection molded specimens were dried under vacuum at 50°C for 32 days. The results of the tensile, flexural and impact tests are listed in Table 5. For comparison, the values determined for the commercial PNC from Ube, PA1015C2 (containing 2-wt% organoclay), are also shown.

4.6 Mechanical properties of the PP-based PNC

Prior to testing the specimens were dried under vacuum at 90°C for 12h. The tensile and flexural test results are listed in Table 6. However, since flexural modulus and strength are linear functions of the tensile modulus and strength, respectively [Error! Bookmark not defined.], only the tensile properties (and $NIRT$) will be discussed. Since it was reported that crystallinity affects the mechanical performance [44], the total crystallinity, X , in the injection-molded, undeformed specimens was measured in a DSC. The results showed that in produced samples the crystallinity is nearly the same: $X = 43 \pm 2\text{-wt\%}$, and the melting point $T_m = 165.0 \pm 0.5^\circ\text{C}$. Thus, for the PNC series discussed in this paper the crystallinity effects on the mechanical behavior might be neglected.

5 Discussion

It is desirable to replace the reactive method for the production of PNC by melt compounding. The replacement will be possible if the process economy and material performance are advantageous. It is difficult to discuss economy in general terms, as there are many synthetic and processing technologies as well as local market influences. Thus, at least one should know under which melt compounding conditions one might obtain similar degree of clay dispersion, and performance as that offered by synthetic methods. The following discussion is divided into two parts focusing on dispersion, and then on its effect on the mechanical performance.

5.1 Clay dispersion in melt compounded PNC

The thickness of the simplest macromolecular stretched chain $-(CH_2)_n-$ is about 0.35 nm [45], thus organoclay with $d_{001} > 1.6$ nm is required – both C10A ($d_{001} = 1.9$ nm) and C15A ($d_{001} \approx 2.5$ nm) fulfill this condition, and in the presence of miscibility (a thermodynamic driving force) the macromolecules should be able to diffuse into the intergallery cavity and exfoliate the clay. However, it is not obvious how to ascertain system miscibility. Most commercial intercalants are quaternary ammonium cations, *i.e.*, C10A = di-methyl, benzyl hydrogenated tallow ammonium chloride (2MBHTA), C15A and C20A = di-methyl di-hydrogenated tallow ammonium chloride (2M2HTA), or C30B = methyl tallow di-ethoxy ammonium chloride (MT2EtOHA). Because of the clay polarity, the methyl, benzyl and ethoxy groups are adsorbed onto the clay surface, and mainly C_{18} -chain interacts with the matrix polymer. Considering the reduced molecular mobility caused by adsorption, the organoclays are immiscible with most thermoplastics, *viz.* PS, PA-6 and PP. Ironically, the thermal instability of ammonium intercalants seems to be required for the intercalation/exfoliation during the melt compounding.

Exfoliated PNC with PS as the matrix have been obtained by either dispersing clay intercalated with vinyl terminated modifier in styrene and polymerizing, or by compounding PS with clay pre-intercalated with ammonium ion terminated PS or its oligomer [46, 47]. Melt compounding of PS with commercial organoclays invariably resulted in poor dispersion, small enhancement of modulus and large reduction of the impact strength. Promising results were obtained by Tanoue *et al.* who added compatibilizer (polystyrene-*co*-vinyl-oxazoline) to PS/organoclay [48]. However, even under the optimized compounding conditions the moderate increase of modulus

(by 12% at 5-wt% clay loading) was accompanied by reduced tensile and impact strength. Poor mechanical performance of PNC seems to be a rule for glassy polymer matrices [49].

Maxwell *et al.* melt intercalated of PA-6 with MMT-2M2ODA and a silane sizing agent in a TSE [50]. These attempts did not result in exfoliation. Dennis *et al.* [27] reported that melt compounding of PA-6 with C30B or with C15A resulted in easy exfoliation for the former, and intercalation for the latter. Similar results were obtained by other authors compounding PA with the “C30B-type” and “C15A-type” organoclays [28,51, 52, 53, 54, 55, 56, 57, 58, 59, 60]. It is instructive to rationalize the mechanisms that lead to these different MMT dispersions in PA matrix. The key properties are listed in Table 7.

Table 7. Comparison of C15A and C30B properties for PA-6 based PNC.

Property	C15A	C30B
Intercalant	2M2ODA	MT2EtOH
Interlayer spacing, d_{001} (nm), of organoclay	2.96	1.86
Intercalant content (CEC)	1.25	0.90
TGA wt loss (% at 250°C)	1.28	1.88
Thermal degradation during compounding (see text)	Less	More
Miscibility with PA-6	Very poor	Poor
Dispersion after compounding PA-6 with 2-wt% organoclay in a TSE	Intercalated, $d_{001} \approx 3.5$ (nm)	Exfoliated

The starting point for the discussion is the results of molecular modeling of PA/organoclay [61, 62]. These showed that the binding energy between PA-6 or PA-66 melt and bare MMT is the highest, linearly decreasing with the volume of incorporated intercalant. In short, neat MMT is miscible with PA. Consequently, in direct compounding of non-intercalated MMT with PA-6 only the insufficient intergallery space prevents macromolecular diffusion and exfoliation. When instead of neat clay an organoclay is introduced into PA matrix the situation is reversed – now the intergallery spacing is sufficient for the diffusion, but the system is immiscible. Only partial removal of the intercalant (*e.g.*, by thermal degradation) offers a chance for the macromolecules to interact with clay surface and improve intercalation []. Both processes, the degradation and the macromolecular diffusion, are rate-dependent. Because of the possibility of clay re-aggregation, it is desirable that the diffusion rate is higher than that of degradation. Of the two organoclay,

C30B has lower thermal stability than C15A [^{63, 64, 65, 66}]; hence would the diffusion rate was the same for C15A and C30B, the former should be expected to lead to higher degree of clay dispersion than the latter. Evidently, the diffusion rate in these systems is not the same – the presence of the polar hydroxyl groups in C30B sufficiently reduces the repulsive effect of the paraffin components for the PA macromolecules to diffuse faster to the bare clay surface and exfoliate the system.

When PA-6/C15A is compounded in a TSE the diffusion rate is too slow for exfoliation, and a dynamic equilibrium is established at $d_{001} \approx 3.5$ (nm). However (see Table 7), compounding in SSE + EFM sufficiently helps the macromolecules to reach the bare clay surface before re-aggregation takes place and produce exfoliated system. At constant throughputs, the residence time in SSE + EFM is longer than that in TSE, but exfoliation is achieved only when sufficiently small gap (*i.e.*, sufficiently high elongational field) is provided.

The importance of the thermodynamic interactions, these between polymer and clay surface or an intercalant, is further demonstrated by the PP-based PNC. Here, only the compatibilizer with polar groups might interact with the bare clay. As the direct comparison of the two organoclays indicated, in the PP + PP-MA matrix the presence of –OH groups of C30B and its poorer thermal stability provide less favorable condition for the diffusion of PP-grafted compatibilizer than that of long hydrogenated tallow groups in C15A (or C20A) – thus higher degree of dispersion is obtained for the latter organoclays [^{63, 64, 65}].

The early attempts to produce PP-based PNC also employed the polymerization route. Alternatively, it was proposed to incorporate ammonium ions at the ends of either the main or side chain of PO macromolecule []. However, both approaches were found impractical. In the 1990's Toyota introduced the compounding method [^{67, 68}]. Exfoliation was reported for systems comprising MMT-ODA and large quantities of “guest molecules” with polar terminal groups (*e.g.*, hydroxyl, acid or anhydride). When the ratio of PP-MA/organoclay was less than 3, only intercalations was observed. It has been shown by FT-IR that maleic anhydride (MAH) groups of PP-MA, react with hydroxyls on the clay surface [⁶⁹].

Melt compounding of PP-based PNC is challenging. Not only PP is immiscible with clay and intercalant, but also the required PP-MA compatibilizer has the tendency of forming clusters

within PP matrix. Thus, for grafting to take place, the intercalant has to be partially removed from the clay surface, the MAH clusters broken, and the PP-MA macromolecules must fast enough diffuse and react with clay surface before the platelets re-aggregate. Furthermore, isotactic-PP matrix is highly crystalline – while crystallinity of PA-6 is about 20 to 30% [70,71], that of PP ranges from 40 to 60% []. This means that in the solidified specimens the clay platelets are highly concentrated within the non-crystalline phase, and on the basis of the geometric arguments, their interlayer spacing is reduced.

The data presented in Figs. 4 and 5 show two measures of clay dispersion for PP-based PNC compounded using EFM with either the TSE, or SSE. The interlayer spacing, d_{001} , in Fig. 4 shows a quite a different behavior for the TSE + GP + EFM than that for SSE with EFM-3 or EFM-N. The reason for the disparity is the residence time, t_R : In the partially filled TSE the reduction of the C-D gap increases t_R , what in turn extends the intercalant degradation and reduces d_{001} . By contrast, in fully flooded SSE at constant Q the residence time rests the same – the effect of intercalant degradation is visible only for the smallest gap: $h \approx 15 \mu\text{m}$.

Compounding in TSE alone yields a relatively high interlayer spacing (the highest value in Fig. 4 for the arbitrarily assumed $h = 4 \text{ mm}$: $d_{001} \approx 3.6 \text{ nm}$) and the lowest degree of exfoliation (the lowest value in Fig. 5: $\Delta E_x = 2$). When EFM is attached to the extruder, the degree of exfoliation increases with reduction of the gap between C-D plates to $\Delta E_x = 28\%$, while the interlayer spacing gradually decreases to about $d_{001} = 2.9 \text{ nm}$. The decrease mainly originates from the intercalant degradation during the increasing residence time. When the system is compounded in SSE + EFM, three zones of the C-D gap can be defined: $h \geq 100$ where d_{001} is constant, $h \approx 30$, where d_{001} has at a local maximum, and $h < 30 \mu\text{m}$ where d_{001} decreases due to high stress-induced intercalant degradation. It is noteworthy that the degree of exfoliation increases in all three zones. Similarly as for PA-6 systems, SSE + EFM-N cause the best clay dispersion.

In short, the use of EFM with TSE or SSE (especially the new EFM-N) for the preparation of PNC is beneficial for clay dispersion. This has been expected as the flow between the C-D plates of EFM engenders three types of flow: the planar elongational at the entrance, the shear inside it, and the orthogonal extensional at the exit. Thus the organoclay stacks are oriented at the entrance to C-D gap, they peel off by velocity gradient within the gap, and then they are “pulled apart” in

the divergent part of C-D. The process is efficient, rapid, and it is repeated several times before the melt exits from the device.

For comparison, the corresponding values determined for the commercial PNC, Ube PA1015C2 are also given. The latter was prepared at high temperature by ring-opening polymerization of ϵ -caprolactam in the presence of MMT pre-intercalated with ω -amino dodecanoic acid (ADA). Thus, the intercalant molecule is the first unit of the PA-6 chain that ionically bonds it to the clay surface [72]. The system is exfoliated, and it has excellent properties. The molecular weight of the PA-6 matrix is $M_n = 22$ kg/mol and the organoclay content 2 wt%; hence similar to that of PA-6 used in these studies. While in 1015C2 the PA-6 macromolecules are directly grafted to clay surface, in PA-6/C15A the immiscible with PA-6 intercalant forms a barrier for direct interactions between the clay surface and polymer. Thus, only after its partial elimination the contact between PA-6 macromolecules and clay surface might be established; this leads to PA-6 adhesion and solidification. Evidently, the differences in chemical structures of 1015C2 and PA-6/C15A might affect the PNC performances.

5.2 Relation between the clay dispersion and PNC performance

The mechanical properties of PS-based PNC are presented in Figs. 6 and 7, while of these with PA-6, and PP + PP-MA matrices are listed in Tables 5 and 6, respectively. The tensile and flexural tests results are linearly related [37, Error! Bookmark not defined.]; hence only the tensile and impact properties need to be considered. There are at least four parameters that characterize clay dispersion, and other four that describe the mechanical properties [Error! Bookmark not defined., 39]. A linear regression analysis was employed to discover which dispersion parameter dominates each mechanical parameter:

$$y = y(x) = a_0 + a_1 d_{001} + a_2 N + a_3 Ex + a_4 Agg \quad (3)$$

where: $y \equiv \{E, \sigma, \epsilon_b, NIRT\}$, and Agg is the relative number of aggregates per surface area of the FEGSEM micrograph []. Summary of this analysis for PNC with PA-6 or with PP + PP-MA is provided in Table 8 (since PS-based PNC showed poor clay dispersion these results are omitted). As the summary indicates, for the well dispersed system such as PA-6/C15A, the relative modulus correlates with d_{001} , while the tensile and impact strength with the degree of exfoliation,

E_x ; no correlation could be found for the elongation at break. For modestly dispersed systems, such as PP-based one, the presence of Agg strongly affects the performance; this is particularly evident for the tensile and impact strength. By contrast with the PA-6/C15A system, in PP-based PNC the modulus shows poor correlation with either d_{001} or E_x , but a good one when both these dispersion characteristic parameters were combined.

Table 8. Main dispersion parameters affecting the mechanical performance

Mechanical Parameter	Matrix polymer	
	PA-6	PP + PP-MA
Modulus, E	d_{001}	d_{001} and E_x
Strength, σ	E_x	N , Agg
Elongation at break, ϵ_b	(not correlating)	--
Notched Izod impact strength at room temperature, $NIRT$	E_x	d_{001} , Agg

Empirically [2], the relative modulus, E_R of exfoliated PNC was found to linearly increase with clay content according to Eq. 2 with $a = 0.2$, therefore for the PA-6 based PNC's with 2-wt% C15A (1.14-wt% clay) the predicted value is $E \leq 3.5 \pm 0.2$ GPa, in good agreement with the experimental value: $E = 3.75 \pm 0.2$ GPa. As the data in Table 5 show, the average values for E for PNC compounded in TSE (with or without EFM) are significantly lower than these from SSE, viz. $E = 3.35$ vs. 3.75 GPa, respectively. The difference most likely originates from a shear-induced degradation of the polymeric chains. Similarly, the predicted modulus for fully exfoliated PP + PP-MA with 2-wt% C15A should be $E \leq 2.1 \pm 0.1$ GPa; surprisingly this value is close to the experimental value of $E = 2.11 \pm 0.04$ GPa determined for samples from TSE or SSE compounding lines [1].

Considering oriented, anisometric particle filled polymeric systems Halpin-Tsai (H-T) derived expression for E_R in the stress direction:

$$E_R \equiv E_c / E_m = (1 + 2p\kappa\phi_f) / (1 - \kappa\phi_f) \quad (4)$$

$$\kappa = (E_f - 1) / (E_f + 2p); \quad E_f \equiv E_f / E_m$$

where E_f and ϕ_f is the filler modulus and its volume fraction, respectively. For clay $E_f = 170$ GPa and $p = 295$ may be used [2], what leads to $E = 3.7 \pm 0.2$ and 2.4 ± 0.2 GPa, for PA-6 and PP + PP-MA, respectively, i.e., in good agreement with the above cited values.

Similarly like modulus, the tensile strength, σ , of PA-6/C15A system is significantly higher in samples compounded in SSE than in TSE (see Table 5), and within the error range of $\pm 4\%$ constant for the PP-based PNC (see Table 6). Again, one can define the relative tensile strength, σ_R , and compare the experimental value with a theoretical prediction. For the continuous particles that perfectly adhere to matrix, the tensile strength in the stress direction is expected to follow the volumetric rule of mixtures [73]:

$$\sigma_R \equiv \sigma / \sigma_m = 1 + \phi_f(\sigma_f - 1); \quad \sigma_f \equiv \sigma_f / \sigma_m \quad (5)$$

where ϕ is the volume fraction, and the subscripts m and f stand for matrix, and filler, respectively [2]. As reported before [], Eq. 5 predicted smaller values of σ_R , than the experimental. The only possible source of this disparity is the volume fraction of the reinforcing particles. The ϕ_f value, calculated from experimental σ_R , for PA-6 and PP-type PNC indicate that the volume of the reinforcing particles is respectively *ca.* 9 and 5 times larger than that of MMT, what implies that, as expected, the clay volume is effectively augmented by adsorbed polymer.

The information from the analysis of the modulus and strength might appear to be conflicting – for the former substituting the bare clay dimension into H-T equation provided good agreement with experiment, whereas analysis of the stress dependencies indicates that the filler particles are substantially augmented by solidified polymers. To solve this apparent conundrum the H-T relation was written for filler particles modified by the adsorbed polymer:

$$\begin{aligned} E'_f &= (E_f + \xi E_m) / (\xi + 1) \\ p' &= p / (\xi + 1) \\ \phi'_f &= \phi_f (\xi + 1) \end{aligned} \quad (6)$$

where the prime (') indicates the modified parameters of H-T dependence, and ξ is the thickness of adsorbed polymer, relative to the clay platelet thickness. The results of calculations show that algebraically, $E'_R \cong E_R$ [].

Table 8 indicates that the impact strength at room temperature (*NIRT*), depends on different dispersion parameters for PA-6 than for PP-based PNC – in poorly dispersed systems the organoclay aggregates control the tensile and impact stress, whereas in well-dispersed one the

level of exfoliation, Ex , is mainly responsible. As data in Fig. 8 for the PA-6 type PNC indicate, compounding in TSE resulted in low Ex and $NIRT$. By contrast, SSE + EFM engendered better exfoliation and impact properties. Again, EFM-N gave better results than its earlier version, EFM-3. The results signify that one needs a relatively high degree of exfoliation ($Ex > 70\%$) for good impact performance.

It is commonly assumed that stiffer polymer has lower elongation at break and impact strength. However, as data in Table 5 indicate, such a correlation is not always found. When all the amassed results for PA-6/C15A are placed on a graph (53 samples) and the least-squares line is computed, the correlation coefficient of $NIRT$ vs. E is $r = 0.1$, indicating that effectively the impact performance is independent of modulus (plot of $NIRT$ vs. σ_b gave $r = 0.54$).

In the Fig. 8, Ube 1015C2 shows low impact strength, especially when the high tensile modulus and strength are taken into account. The difference between this PNC and PA-6/C15A systems originates from the clay-matrix interphase. In reactively prepared 1015C2 the clay platelets are ionically bonded to the matrix through C_{12} chain, whereas in PA-6/C15A there are delocalize polar interaction. Thus, the PA-6/C15A is less rigid, but tougher than the commercial PNC.

Fig. 8. Notched Izod impact strength at room temperature ($NIRT$) vs. exfoliation for PA-6/C15A; the data point for Ube PA1015C2 is also shown. The mean error of $NIRT$ is 2.04 J/m.

6 Conclusions

In this paper the influence of the degree of clay dispersion on mechanical performance of three PNC series (based on PS, PA-6 and PP) was discussed. These systems were melt-intercalated in compounding lines consisting of either TSE with GP and EFM, or SSE with EFM. The master-batch (MB) method was employed.

Consistently the SSE + EFM-N compounding line engendered better performance than TSE with or without EFM; especially the EFM-N was efficient in peeling off individual lamellae from the short stacks. In spite of shorter residence time, TSE caused more intercalant degradation than

SSE + EFM. Compounding PA-6/C15A in the SSE + EFM resulted in full clay exfoliation – similar to that in commercial PA1015C2. In TSE + GP + EFM the dispersion was significantly poorer. The results for the PS or PP-based PNC's were less impressive. However, again better dispersion was obtained in SSE + EFM than TSE + GP + EFM. Compounding with newly designed EFM-N led to better dispersion than that with the commercial EFM-3.

Several process variables were studied, viz. temperature, screw speed, throughput, method of extruder feeding, composition, organoclays, compatibilizers, pressure inside EFM, gap between the C-D plates, etc. The two compounding lines, with TSE or SSE, were compared at the same throughput of $Q = 5$ or 10 kg/h.

Considering immiscibility of organoclay with the matrix polymer, the mechanism of organoclay dispersion seems to involve two steps: (1) a partial elimination of the intercalant from clay surface, followed by (2) clay-matrix interaction. For the PS system the Hofmann elimination mechanism resulted in a progressive collapse of the interlayer spacing – evidently, the interactions between clay surface and PS macromolecules is insufficient to prevent re-aggregation. For the PA-6 based PNC the second process involves strong polar interactions between clay and the matrix, which leads to adsorption of PA-6 on the surface and its solidification – when suitable compounding conditions are provided, exfoliation might be obtained for any organoclay having sufficient interlayer thickness, $d_{001} > 1.6$ nm.

In the case of PP-based PNC, interactions between bare clay surface and PP are worse than these with PS, thus compatibilization is essential. However, since the interactions of clay with ammonium ions are stronger than these with PP-MA, the progressive decomposition of intercalant eventually might result in re-aggregation. It is also noteworthy that effective volume fraction in PP-based PNC is significantly smaller than this in PA-6/C15A systems, viz. 5 vs. 9, i.e., the thickness of solidified layer in the former system is 2 nm, whereas in the latter twice as large. The difference again points out poorer interaction of clay with PP-MA than with PA-6.

The concentration dependence of the tensile modulus for the PNC with either PA-6 or PP was close to values calculated from an empirical as well as from the Halpin-Tsai relations, i.e., the about 23% increase of modulus at 2-wt% organoclay loading. By contrast, the modulus increase in PS matrix was modest, suggesting a micro- not nano-composite behavior. Furthermore, the tensile strength of the PA-6 and PP based PNC was higher than predicted by the most optimistic

relation. This extra enhancement originates from the increased volume of reinforcing particles, caused by solidified the matrix polymer adsorbed onto the clay surface.

The mechanical performance of the PP-based PNC is puzzling as here the organoclay is crowded in the non-crystalline phase forming intercalated stacks. However, the mechanical properties are enhanced nearly as much as by exfoliated platelets.

7 Appendix

7.1 Abbreviations

2M2HTA	di-methyl di-hydrogenated tallow ammonium chloride
2MBHTA	di-methyl, benzyl hydrogenated tallow ammonium chloride
ADA	ω -amino dodecanoic acid
ASTM	The American Society for Testing and Materials
C10A	Cloisite ® -10A = MMT-2MBHTA
C15A	Cloisite ® -15A = MMT-2M2HTA
C20A	Cloisite ® -20A = MMT-2M2HTA
C30B	Cloisite ® -30B = MMT- MT2EtOHA
C-D	convergent-divergent plates
CEC	cation exchange capacity
CORI	co-rotating, fully intermeshing TSE
DEFM	dynamic extensional flow mixer
EFM	extensional flow mixer: EFM-3 and EFM-N are, respectively, commercial mixer for blending, and new version for dispersing nanocomposites
FEGSEM	scanning electron microscopy with cold field emission gun
FT-IR	Fourier transform infrared spectroscopy
GP	gear pump
HRTEM	high-resolution transmission electron microscopy
HT	hectorite
L/D	length to diameter ratio
MAH	maleic anhydride
MM	molecular mechanics
MMT	montmorillonite
MT2EtOHA	methyl tallow di-ethoxy ammonium chloride
NIRT	notched Izod impact strength at room temperature (J/m)
PA-6	polyamide-6
PET	polyethylene terephthalate
PNC	polymeric nanocomposites
PO	polyolefin
PP	polypropylene
PP-MA	maleated-PP
PS	polystyrene
RTD	residence time distribution
SCF	self-consistent mean field
SSE	single-screw extruder
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TSE	twin-screw extruder
XRD	X-ray diffraction

7.2 Symbols

Agg	relative number of aggregates observed under the FEGSEM
C_{clay}	clay concentration
d	equivalent clay platelet diameter
d_{001}	interlayer spacing (nm)
E	tensile modulus (GPa)
E_f	filler modulus
E_F	flexural modulus (GPa)
E_R	relative tensile modulus = $E(PNC)/E(matrix)$
Ex	exfoliation (%)
G	toughness (J)
h	gap between C-D plates (μm)
L/D	length to diameter ratio
MB	master batch compounding method
M_n, M_w	number, weight-average molecular weight
N	the number of platelets per stack, or screw speed
$NIRT$	notched Izod impact strength at room temperature (J/m)
p	the average aspect ratio of clay platelets
Q	throughput (kg/h)
r	correlation coefficient
SP	single-step compounding method
t	clay platelet thickness
T, T_m	temperature, melting point ($^{\circ}C$)
t_R	residence time (s)
t_S	the thickness of the diffracting clay stack
V, V_{enc}	actual and encompassed volume
w	is the organoclay content in wt%
X	crystallinity content: (%)
σ	tensile strength at yield (MPa)
ΔEx	excess exfoliation over that of the organoclay (%)
ΔG_m	Gibbs free energy of mixing
ϵ_b	elongation at break (%)
ϕ, ϕ_c	volume fraction, and its critical value
ϕ_f	filler volume fraction in PNC
λ	viscosity ratio
σ_b	the tensile strength at break (MPa)
σ_F	flexural yield strength (MPa)
σ_f, σ_m	filler, matrix tensile strength (MPa)
ξ	adsorbed polymer thickness = (thickness of adsorbed polymer)/(clay platelet thickness)

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