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Extensional flow mixer for polymer nanocomposites

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Abstract

The Extensional Flow Mixer (EFM) has been used in the plastics industry, e.g., for homogenization of reactor products, preparation of polymer blends, or incorporation of a plasticizer. Recently there were several laboratory attempts to use EFM for the preparation of polymeric nanocomposites (PNC) by dispersing organoclay in a polymeric matrix. Usually, for this purpose the EFM was mounted on a twin-screw extruder (TSE) equipped with a gear pump (GP). The use of EFM resulted in improved dispersion and performance – more significant in polyamide or thermoplastic polyester, but marginal in a polyolefin or polystyrene. To improve EFM efficiency, the standard device was modified, by redesigning the convergent-divergent plates that engender the extensional flow. The two mixers, the commercial EFM-3 and the new EFM-N, were evaluated using a single-screw extruder (SSE). Two systems were examined: (1) polyamide-6 (PA-6) with Cloisite®-15A (C15A), and (2) polypropylene (PP) with maleated-PP (PP-MA) and C15A. The compounded samples were injection molded, and then tested for the degree of dispersion, and mechanical performance (tensile, flexural, and impact). The results demonstrated superiority of the new EFM-N. Compounding PA-6 with C15A in SSE + EFM-N fully exfoliated the organoclay, producing PNC with high performance (e.g., the tensile modulus of PNC containing 2-wt% of C15A was higher by 30% than that of the PA-6 matrix), comparable or better than a commercial nanocomposite produced by polycondensation of ϵ -caprolactam in the presence of clay, pre-intercalated with reactive cations.

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1. Introduction

Currently, the production of the polymeric nanocomposites (PNC) is based mainly on the reactive method, i.e., polymerization of given monomer(s) in the presence of pre-intercalated mineral or synthetic clay [Okada and Usuki, 1995]¹, [Goettler and Recktenwald, 1998]², [Utracki, 2004]³. Only the resin manufacturers able to dedicate at least one production line to PNC may use this method. Development of reliable, simple melt compounding methods would shift the PNC production to compounders and fabricators of finished products, i.e., where most multicomponent systems are produced [Utracki, 2002]⁴. This technology evolution will add flexibility; nanocomposites with desired performance characteristics will be prepared just before use. The technological advantages will greatly accelerate introduction of these new materials into the market.

The polymeric nanocomposites (PNC) are relatively recent commercial materials, growing at an annual rate of 18.4% (from 195 million US\$ in 2004 to 311 million in 2008) [Brauer, 2004]⁵. The main application of PNC is in the automotive industry (GM, Mitsubishi, Toyota). The projected consumption in the USA is to increase by 2009 to 550 kton/y [Ruban *et al.*, 2000]⁶, with the growing demand for packaging, appliances, building & construction, electrical & electronic, lawn & garden, power tools, etc. Currently, the cost differential between the neat polyamide matrix and its PNC is about 10%.

Rheology distinguishes two classes of flow: (1) the shear, characterized by the presence of vorticity and (2) the extensional or irrotational. Most mixers and plastics processing machines operate in shear – the elongational component is present only in the regions where the flow lines are not parallel to each other. However, it has been theoretically shown that dispersing in shear is energetically inefficient, and for blends it is limited to relatively low value of the component viscosity ratio. Extensional flow mixing offers several advantages over that in shear:

1. It is orders of magnitude more energy-efficient than shear
2. It generates better dispersive and distributive mixing
3. The temperature increase in extensional flow is ca. 1 to 3°C
4. It does not cause re-aggregation of solid particles reported for shear
5. It can be economically generated using convergent-divergent flow geometry, either in form of motionless or dynamic mixer.

These reasons induced NRCC/IMI to develop the Extensional Flow Mixer (EFM)⁷. The device was designed as an inexpensive mixer for blending, alloying, or homogenizing molten polymers, when attached to a single-screw extruder (SSE). This type of extruder is known to be able to melt and pump polymers, but it is a notoriously poor mixer. Furthermore, as a purely shearing device, it may locally shear heat the melt to temperatures exceeding the set one by as much as 70°C (measured) and cause a thermo-mechanical degradation of polymer. Alternatively, a twin-screw extruder (TSE) with a gear pump (GP) may be used. TSE offers more controllable mixing, but at a much higher capital and operational costs than SSE⁸. The need to generate sufficient pressure implies that GP must be used – with additional cost, and problems associated with this device. For the preparation of polymer blends, the system SSE + EFM has been found not only ten times less expensive, but also it often outperformed TSE in such applications as elimination of gel particles in film resins, incorporation of elastomer into thermoplastic, or blending two polymers such as PET with PP or PS with PE [Utracki and Luciani, 1996]⁹; [Luciani and Utracki, 1996]¹⁰. These results were expected on the basis of theoretical analysis of mixing. Indeed for melt homogenization, and melt blending EFM performs well. However, the theory of dispersing one molten polymer in another is fundamentally different from that describing dispersing aggregates of solid particle.

The EFM is the only mixer on the market that uses extensional flow field to ascertain mixing. In 1999 IMI licensed the mixer to the Extensional Flow Mixer, Inc., for the manufacturing and distributing the EFM¹¹. The license was withdrawn in the early 2004.

During the last few years the use of the commercial EFM-3 for dispersing organoclay in polar thermoplastic matrices (PET and PA-6) gave surprisingly good results¹². The theory of mixing suggests that the dispersion of solid particles should be four times more efficient in the extensional flow than in a shear field [Manas-Zloczower and Tadmor, 1994]¹³. Compounding PET with 4-wt% of organoclay in TSE + GP + EFM-3 improved the tensile modulus by ca. 70%, i.e., about 10% less than predicted for fully exfoliated system [Garcia-Rejon and Simard,

2002]¹⁴, [Song, 2002]¹⁵. However, attempts to disperse organoclay in non-polar polymers (e.g., PP, or PS) in TSE with GP and commercial EFM-3 were less successful [Tanoue *et al.*, 2003; 2004; 2005]^{16, 17, 18}.

These preliminary uses of EFM for generating PNC indicated that: (1) the equilibrium thermodynamics decides whether exfoliation is possible or not; (2) compounding has the kinetic role – it facilitates exfoliation provided that the system is thermodynamically miscible; and (3) owing to a different dispersive mechanism of organoclay aggregates than that of one liquid in another the flow geometry, i.e., the shape of the convergent-divergent plates (C-D) inside the EFM must be redesigned.

There is a growing demand to make EFM more universal, applicable for the dispersing a diversity of nanoparticles, viz. clay, organoclay, carbon nanotubes (CNT), carbon whiskers (CW), carbon black (CB) or silica gel. Thus, designing new convergent-divergent (C-D) geometry for nanocomposites is needed. The key to it is the understanding of flow and orientation of the nanoparticle aggregates, the necessary sequence and intensity of extensional and shear stress fields.

In this paper we present results of the collaborative research program between the Japan Steel Works Ltd. (JSW) and NRCC/IMI in designing, manufacturing, and testing EFM with new C-D geometry, which in the following text is labeled as EFM-N. This extensive tests program involved compounding of two types of PNC, at a variety of compositions, under diverse processing conditions. Owing to space limitation, here we shall focus primarily the use of SSE for continuous production of PA-6 based fully exfoliated PNC. For the sake of comparison, the results from SSE + EFM-N will be compared with those of SSE + EFM-3, as well as with the data generated using TSE + GP, with or without EFM.

2. Experimental

2.1. Compounding

The characteristics of materials used in these studies are shown in Table 1. The two-stage compounding was carried out under a blanket of dry N₂. At the first stage a master-batch (MB) was prepared in a TSE, feeding the matrix polymer from the main hopper, and C15A from a side feeder. The set barrel temperatures were: $T = 180$ and 200°C for PP, and 240°C for PA-6 system. The second stage involved diluting MB with appropriate polymer(s), using either a SSE (Flag 63.5 mm, L/D = 24, with Dry mixing element), or Leistritz-34mm TSE (corotating, L/D = 40,

screw speed of $N = 200$ rpm, throughput of $Q = 5$ and 10 kg/h). The EFM (either the commercial EFM-3 shown in Figure 1, or the new EFM-N) was directly attached to SSE, and with an intermediary GP (Maag Pump System Model EH 45/28) to TSE. The EFM was operated with the gap between C-D plates set at: $h = 5, 15, 30, 63.5, 100, 300, 1016, \text{ and } 2000 \mu\text{m}$. To prepare the test specimens Engel 150T injection-molding machine was used with ASTM end-gated mold.

Table 1. Material characteristics

Material	Trade name ¹	M_w (kg/mol)	Density (g/mL)	$T_m(^{\circ}\text{C})$	MAH (wt%)	Supplier
PA-6	Ube-PA1015B	21.7	1.14	216	--	Ube Industries
PP	PROFAX-PDC1274	250	0.902	161	--	Basell Polyolefins
PP-MA1	Epolene-3015	47	0.91	162	1.31	Eastman Chemicals
PP-MA2	Polybond 3150	330	0.91	164	0.5	Crompton
Organo-clay (C15A)	Cloisite® 15A	--	--	--	--	South. Clay Prod.

Notes: ¹ Abbreviations used in the text (from top): PA-6, PP, E3015, P3150, and C15A; ² C15A is MMT intercalated with excess (1.25 meq/g or 0.78 mmol/g) of di-methyl di-hydrogenated tallow ammonium chloride (Arquad 2HT); it contains 43 wt% of the organic phase and 2-wt% of water

In EFM the melt stream from an extruder is directed to the rim of the C-D platelets, and then it flows in the gap between them, exiting through the central hole (see Figure 1). This third in series design, EFM-3, has the spiral mandrel that offers several advantages: (1) sturdy design, with minimum of pressure-caused deflection, (2) homogenization of the melt temperature, (3) uniform melt distribution to the annular space around the convergent-divergent plates, (4) minimal modification of flow stream morphology, and (5) low pressure consumption. The unit proved itself on the production lines. The same sturdy construction is used for EFM-N, the only difference being the geometry of the C-D plates.

Prior to PNC compounding, the in-line measurements of the residence time distribution (RTD) were conducted using ultrasonics (US)¹⁹ to detect a small amount of CaCO_3 added to molten polymer as a tracer. The mean residence time is listed in Table 2. The compounding as well as the RTD tests were conducted at constant throughputs, e.g., $Q \cong 5$ or 10 kg/h, in SSE as well as in TSE. However, while in TSE the throughput is controlled by the feed rate, in SSE this is accomplished by the screw speed. Thus, while the residence time in TSE changes with flow

restrictions in the die region that in SSE is constant within the range of experimental error, viz. $Q = 5.21 \pm 0.33$ kg/h. Evidently, increasing the throughput in SSE by a factor n , reduces the mean residence time by n .

Figure 1. Commercial EFM-3 from EFM Inc., Mississauga, ON, Canada. The unit uses the spiral feed for better temperature control of the feed stream control and added rigidity.

Table 2. Time to attenuation peak during compounding at constant throughput of $Q = 5$ kg/h in TSE or SSE compounding lines.

Twin-screw extruder		Single-screw extruder	
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

4.1. Testing

The degree of clay dispersion was determined using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM; Hitachi H9000), and scanning electron microscopy (Hitachi S4700 with cold field emission gun, FEG-SEM). The specimens were prepared by cryo-shaving ca. 80 nm thick flakes from the narrow section of dogbones using a Leica Ultracut FC microtome with diamond knife. The sections were transferred from water to 200-mesh Cu grids.

XRD measurements were carried out using a Brüker D8 Discover with $\text{CuK}\alpha$ radiation. XRD scans were obtained using an incident X-ray wavelength $\lambda = 0.15406$ nm at a scan rate of $0.3^\circ/\text{min}$. The specimens were mounted horizontally. The spectra were obtained using slits of 1.0, 0.1, and 0.6 mm, sweeping the angles from 0.8 to 10° . From the spectra three measures of the degree of dispersion were calculated: (1) the mean interlayer spacing, d_{001} , (2) the number of platelets per stack, and (3) the relative amount of clay platelets absent in stacks.

The tensile and flexural tests (ASTM D638 and D790, respectively) were carried out using an Instron 5500R model 1125 tester. Young's modulus was calculated by least square fitting of the experimental stress vs. strain data, within the initial strain region of $< 0.2\%$. For the flexural tests the support span was 59 mm. Notched Izod impact tests (ASTM D256) were performed at room temperature using an Instron Model 8200 impact tester. The property values reported here represent an average of ten tests for each specimen. Before testing, the PA-6 specimens were dried under vacuum at 50°C for at least 31 days.

3. Results

The compounding conditions for dispersing C15A in PA-6 are provided in Table 3. Similar set of test (but at different temperature) was conducted for the system of PP/PP-MA/C15A. The compatibilizing mixture, PP-MA, comprised equal amount of PP-MA1 and PP-MA2 (see Table 1). For C15A content of $X\text{-wt}\%$, the amount of PP-MA was $2X$. In this publication only compositions containing $2\text{-wt}\%$ of C15A will be discussed. Since the average aspect ratio of clay platelets is $p = 287 \pm 9$, their free rotation would be impossible at higher loading²⁰.

Table 3. Compounding of PA-6/C15A

Test No.	Composition (wt%)		Compounding equipments	EFM gap $h(\mu\text{ m})$	Barrel set T(°C)	Screw speed N (rpm)	Measured throughput (kg/h)	Motor Power(kW)	Specific energy (kWh/kg)	Residence time (s)
	PP	C15A								
PA -0	98	2	SSE	-	240	6	5.5 ± 0.1	0.025	0.005	1163
PA -1			SSE+ EFM-3	15	235	60	6.0 ± 0.3	1.232	0.246	1108
PA -2			SSE+ EFM-N			101	5.1 ± 0.5	2.904	0.581	
PA -3			SSE+ EFM-3	30	240	44	5.1 ± 0.4	0.904	0.181	1138
PA -4			SSE+ EFM-N			82	4.6 ± 0.3	2.021	0.404	
PA -5			SSE+ EFM-3	100		25	5.3 ± 0.4	0.411	0.082	1071
PA -6			SSE+ EFM-N			45	5.1 ± 0.6	0.924	0.185	
PA -7			SSE+ EFM-3	300		8	4.8 ± 0.1	0.066	0.013	1147
PA -8			SSE+ EFM-N			14	5.2 ± 0.2	0.230	0.046	
PA -9	100	0	SSE+ EFM-3	15	230	80	5.2 ± 0.2	1.643	0.329	1108
PA -10			SSE+ EFM-N			101	3.4 ± 0.6	2.904	0.581	
PA -11			SSE	-		8	5.4 ± 0.2	0.066	0.013	1163

Table 4 summarizes the results of the tensile, and impact tests, as well as the XRD measurements. The tensile properties are characterized by four parameters: the Young's modulus, E (GPa), strength at yield, σ (MPa), strength at break, σ_b (MPa), and elongation at break, ε (%). The notched Izod impact strength at room temperature, $NIRT$ (J/m), is listed next. The flexural test data are not listed, since both the modulus and strength was found to correlate to the tensile parameters – see Figure 2.

The X-ray diffraction scans (e.g., see Figure 3) is characterized by three parameters: the interlayer spacing, d_{001} (see Eq. 1), average number of platelets per stack, N (see Eq. 2), and the level of exfoliation, X_E , from the area under the peak, compared to that under the peak of a given organoclay. The Bragg's formula is:

$$d_{00n} = n\lambda / (2 \sin \theta) \quad (1)$$

where, n is an integer, θ is the angle of incidence (or reflection) of X-ray beam. From the peak broadening the thickness of the diffracting clay stack, t_s , may be calculated using Scherrer relation. Knowing this value and d_{001} , the number of clay platelets per average stack is:

$$N = 1 + t_s/d_{001}, \text{ where: } t_s \cong 0.9\lambda/(B_{1/2}\cos\theta_B) \quad (2)$$

where $B_x \cong \theta_1 - \theta_2$ is peak width at half height ($I_{\max}/2$), and $\theta_B \cong (\theta_1 + \theta_2)/2$.

Figure 4 displays HRTEM micrographs of three compounded samples: PA-0, PA-3 and PA-4, containing 2-wt% of C15A and extruded in: SSE, SSE + EFM-3, and SSE + EFM-N. For the extrusion with EFM the C-D gap = 30 μm was used. It is noteworthy that in PA-0 extruded without EFM, a significant degree of exfoliation takes place, but at the same time relatively large organoclay stacks still remain. Addition of EFM-3 or EFM-N virtually eliminates the stacks and increases the degree of exfoliation above the value obtained for the Ube PA1015C2.

Table 4. Tensile, impact, and XRD data for PA and PA based PNC prepared by SSE + EFM

Sample	SSE with	C-D gap h (μm)	C15A (wt%)	Tensile properties				NIRT (J/m)	XRD results		
				E (GPa)	σ (MPa)	σ_b (MPa)	ε (%)		d_{001} (nm)	X_E (%)	N
Ube 1015C2	-	-	2	3.81	94.1	-	65.2	24.0	5.33	80.7	2.44
PA-0	-	-	2	3.66	91.0	66.7	56.4	26.0	3.66	90.5	3.44
PA-1	EFM-3	15	2	3.69	92.0	61.6	115	31.9	3.66	83.7	3.32
PA-3	EFM-3	30	2	3.73	91.3	64.5	123	28.7	3.65	89.9	3.14
PA-5	EFM-3	100	2	3.61	90.2	66.1	148	25.7	2.52	91.5	3.46
PA-7	EFM-3	300	2	-	-	-	-	-	3.69	84.8	3.27
PA-10	EFM-N	15	0	3.03	82.6	63.3	184	34.2	-	-	-
PA-2	EFM-N	15	2	3.72	90.9	65.4	147	32.6	4.83	96.2	2.42
PA-4	EFM-N	30	2	3.77	89.6	60.3	92.8	25.6	4.65	97.1	2.14
PA-6	EFM-N	100	2	3.74	90.2	62.2	65.2	28.3	3.96	86.7	3.15
PA-8	EFM-N	300	2	-	-	-	-	-	3.74	86.9	3.22

Figure 2. Flexural vs. tensile parameters for PA-6, PP, and their CPNC: left plot for moduli, right one for the strength at yield.

Figure 3. The XRD scans for C15A, the master batch (4-wt% C15A), and (for comparison) of the commercial Ube PA1015C2 PNC. To illustrate the effects of compounding the results of compounding in a TSE, in TSE + GP + EFM-3, and in SSE + EFM-N are shown (for the latter runs the C-D gap = $30 \mu\text{m}$ was used).

Figure 4. TEM micrographs of cryo-microtomed PNC's of PA/C15A compound prepared using: A = SSE (PA-0), B = SSE + EFM-3 (PA-3; C-D gap = 30 μm), and C = SSE + EFM-N (PA-4; C-D gap = 30 μm). The magnification was $\times 300k$; 50 nm bar is displayed.

4. Discussion

4.1. Effect of C-D gap on clay dispersion

In Figure 5 the variation of d_{001} , X_E and N with EFM gap for PA-6 based PNC's are presented. Within the range of experimental error, for EFM-3 these three parameters remain relatively constant, whereas for EFM-N both d_{001} , and X_E increase with a decrease of EFM gap. Extrusion of PA-6 with 2-wt% C15A through SSE + EFM-N with large C-D gap leaves behind short stacks with the number of clay platelets per stack, $N = 3.2 \pm 0.1$, similar to the value calculated for SSE + EFM-3. Only when the C-D gap is small, $h = 30 \mu\text{m}$, N decreases to 2.1, and at the same time the degree of exfoliation increases to the observed maximum of $X_E = 97.1 \%$. Further decrease of gap to 15 μm did not improve the dispersion, probably due to short residence time within the high stress region of flow.

In Figure 6 similar information is displayed for the PP-based CPNC. Excepting the smallest gap, $h = 15 \mu\text{m}$ (where degradation causes a collapse of the interlayer spacing), $d_{001} \cong 3.45 \pm 0.05 \text{ nm}$, and $N \cong 3$, are independent of gap. Only the degree of exfoliation smoothly increases with C-D gap reduction – more significantly for EFM-N than for EFM-3.

Figure 5. Variation of d_{001} , Exf and N with EFM gap for PA-6 based CPNC.

Figure 6. Variation of d_{001} , Exf and N with EFM gap for PP-based CPNC. The first point at inverse gap of $1/h = 1/1000$ represents the values obtained using SSE without EFM.

The data in Figures 5 and 6 show a significant difference in the ability of EFM to disperse the same organoclay in PA-6 and in PP + maleated-PP matrix. Using SSE + EFM-N the former system became virtually fully exfoliated. This is particularly significant, since the simultaneously

measured degree of exfoliation in Ube PA1015C2 is lower. The latter PNC has been prepared by dispersing organoclay (montmorillonite pre-intercalated with ω -amino dodecyl acid, ADA) in ϵ -caprolactam, and then polymerizing the suspension. In this process the matrix is covalently bonded to clay via ADA, which becomes the first unit of the macromolecular chain [Okada *et al.*, 1988]²¹, [Okada and Usuki, 1995]²², [Fukui *et al.*, 1992]²³, [Usuki *et al.*, 1996]²⁴.

By contrast with the reactively produced PA1015C2, the PNC prepared by compounding PA-6 with C15A has more complex structure, which is reflected in the mechanical performance. According to the manufacturer, C15A has 25% excess of the intercalant, *di-methyl di-hydrogenated tallow ammonium chloride*, and the organoclay is in form of clay platelet aggregates covered with thick layer of paraffins. Evidently, such a compound would be immiscible with PA-6. C15A at $T > 180^\circ\text{C}$ undergoes the by Hofmann elimination²⁵:

that exposes clay surface. However, as Tanaka and Goettler [2002]²⁶ showed the pristine clay has the highest binding strength with polyamide-66, the conclusion confirmed one year later for PA-6 [Fermeglia *et al.*, 2003]²⁷. Thus, during the PA-6/C15A compounding at 240°C removal of the intercalant is accompanied by diffusion of PA-macromolecules to the bare surface, which leads to progressive exfoliation from the outside of the organoclay aggregate toward the center. In this process there is not a unique covalent bond between PA-6 macromolecule, but rather interaction with dislocated charge. Furthermore, it is unlikely that the Hofmann elimination runs to completion. Thus, the immiscible domains of paraffin-covered clay must co-exist with the areas of direct clay-polymer interactions. Such a system is expected to be less rigid than PA1015C2 with direct covalent bonds, and at the same time more tough.

4.2. Relationships between different measures of the mechanical performance

Figure 2 shows that flexural and tensile properties are inter-related, viz.:

$$F = 0.9996E - 0.0365; \quad r = 0.988 \quad (3)$$

$$\sigma_F = 1.73\sigma - 1.35; \quad r = 0.993 \quad (4)$$

Thus, since the moduli range from about 1.5 to 4.0 GPa, Eq. 3 may be written as $F \cong E$. Similarly, Eq. 4 may be approximated by: $\sigma_F \cong \sqrt{3} \sigma$. It is interesting (see Figure 7) that in both

modes of deformation the yield strength increases with modulus. A common dependence is observed for neat PA-6, and its PNC's prepared in TSE or SSE compounding lines. The highest values of strength and modulus were obtained for the commercial Ube PA1015C2.

Figure 7. Yield strength vs. modulus in tensile and in flexural tests for PA-6, and its PNC prepared in TSE or in SSE + EFM.

Figure 8. Notched Izod impact strength, $NIRT$ (J/m), for PA-6 and its CPNC's vs. the tensile modulus (E); all data are plotted.

The impact strength, $NIRT$ (J/m), is difficult to correlate with either tensile or flexural parameters. However, as the data in Table 4 show, addition of organoclay increased $NIRT$ values. This is in contrast with most reported data, where addition of organoclay reduces the impact strength [Wu *et al.*, 2004]²⁸. Figure 8 shows an empirical correlation between $NIRT$ and E – smaller is the modulus higher is the impact strength. The data for PNC prepared in SSE compounding line indicate that the smaller the C-D gap, the higher the $NIRT$. It is noteworthy that the data point for Ube PNC falls on the same line, computed for SSE + EFM, and as expected, being the most rigid it shows the lowest impact strength.

4.3. Relation between the degree of clay dispersion and mechanical properties

In the preceding parts three parameters that characterize clay dispersion and six parameters describing the mechanical properties were discussed. Since a linear dependence between the tensile and flexural test results exists, the following relationships might now be examined: $y \equiv \{E, \sigma, l\}$ vs. $x \equiv \{d_{001}, N, Exf\}$. To facilitate the task, a linear regression analysis was used:

$$y = a_0 + a_1 d_{001} + a_2 N + a_3 X_E \quad (5)$$

General results are presented in Table 5, individual in Figures 9 and 10, for the tensile modulus and strength, respectively.

Figure 9. Modulus vs. interlayer spacing – symbols 3(x), and N(x) indicate type of EFM with x being the gap in μm . Figure 10. Calculated vs. experimental measures of the tensile modulus – see Table 5.

The regression analysis indicates that the tensile modulus depends on d_{001} , and to a small degree on X_E , but not on N . Plot of Y vs. d_{001} in Figure 9 shows that within the range of experimental errors the observed linear dependence includes the commercial nanocomposite, Ube PA1015C2. At 2-wt% organoclay loading, the relative modulus, $E_R = E(\text{PNC})/E(\text{PA-6}) = 1.3$ agrees with the Halpin-Tsai prediction for oriented PNC. It is noteworthy, that for similar system Shah and Paul [2004]²⁹ obtained $E_R = 1.12$ – only for high molecular weight matrix ($M_n = 29.3$ kg/mol) the authors achieved $E_R = 1.30$.

Table 5. Correlation between the mechanical performance and the degree of clay dispersion in PA-6 matrix

Parameter	y4	y3	(y3)	y2
Modulus vs.:	d_{001}, N, Exf	d_{001}, Exf	d_{001}, N	d_{001}
Standard deviation (σ)	31.05	30.44	32.52	29.69
Correlation coefficient squared (r^2)	0.999965	0.999958	0.999952	0.999952
Coefficient of determination (CD)	0.855088	0.825973	0.801363	0.801331
Correlation	0.924710	0.908831	0.895189	0.895171
a_0	4080 $\pm$ 549	3620 $\pm$ 193	3471 $\pm$ 237	3464 $\pm$ 52
a_1	32.08 $\pm$ 35.84	61.89 $\pm$ 13.10	62.04 $\pm$ 27.29	62.71 $\pm$ 12.74
a_2	-56.8 $\pm$ 63.4	0	-1.31 $\pm$ 46.1	0
a_3	-3.63 $\pm$ 2.98	-1.71 $\pm$ 2.03	0	0
Strength vs.:	d_{001}, N, Exf	d_{001}, Exf	d_{001}, N	Exf
Standard deviation (σ)	0.891	0.797	1.169	0.934
Correlation coefficient squared (r^2)	0.999953	0.999952	0.999897	0.999921
Coefficient of determination (CD)	0.770985	0.770657	0.507097	0.622266
Correlation	0.878058	0.877871	0.712107	0.788838
a_0	104 $\pm$ 16	105 $\pm$ 5.1	73.6 $\pm$ 8.5	109 $\pm$ 5.6
a_1	0.690 $\pm$ 1.028	0.618 $\pm$ 0.343	2.205 $\pm$ 0.981	0
a_2	0.138 $\pm$ 1.817	0	2.944 $\pm$ 1.66	0
a_3	0.184 $\pm$ 0.086	-0.188 $\pm$ 0.053	0	-0.195 $\pm$ 0.062
NIRT vs.:	d_{001}, N, Exf	d_{001}, Exf	d_{001}, N	Exf
Standard deviation (σ)	3.84	3.64	3.653	3.326
Correlation coefficient squared (r^2)	0.990585	0.989422	0.989362	0.989419
Coefficient of determination (CD)	0.129199	0.021617	0.016082	0.021361
Correlation	0.359442	0.147027	0.126816	0.146154
a_0	-23.6 $\pm$ 67.9	20.96 $\pm$ 23.14	21.0 $\pm$ 26.6	20.7 $\pm$ 19.8
a_1	2.84 $\pm$ 4.43	0.057 $\pm$ 1.57	0.641 $\pm$ 3.07	0
a_2	5.51 $\pm$ 7.84	0	1.44 $\pm$ 5.18	0
a_3	0.266 $\pm$ 0.369	-0.074 $\pm$ 0.243	0	0.080 $\pm$ 0.221

Similar analysis indicates that the tensile strength, σ , depends on X_E , with d_{001} having a secondary influence. As the Table 5 indicates, the correlation for σ is poorer than that for E . However, the worst correlation was obtained for the elongation at break and NIRT – here hardly any correlation could be found with the dispersion parameters. In all cases the error of the equation constant was larger than its value! Clearly, the ultimate performance for PA-6 based PNC is dominated by some other physical quantity than the degree of clay dispersion.

At the constant C15A content of 2-wt%, the PP-based PNC's display a narrow range of variables, viz. d_{001} = 3.09 to 3.48 nm, N = 2.64 to 3.1, X_E = 0 to 29%; and similarly: E = 2.01 to

2.09 GPa, $\sigma = 35.4$ to 36.1, $N/RT = 32.5$ to 35.5 (J/m). Owing to the experimental errors, correlations between these two groups are generally poor, viz. $CD = 0.27$ to 0.42. Indeed, the regression analyses indicate that the tensile modulus and NIRT hardly depend on the degree of clay dispersion – other factors seem to control these properties. The exception is the tensile strength at yield, σ , which decreases with increase of N (see Figure 11). Such a behavior at the yield strain can be justified considering that the maleic anhydride groups of PP-MA can easier react with the exposed clay surface outside the stack, than inside it. Thus, larger is the number of clay platelet in stack, weaker is the aggregate; hence the PNC.

Figure 11. Tensile strength of PP-based PNC vs. number of clay platelets per average short stack. The highest value of s is for PNC extruded through SSE + EFM-N (C-D gap = 30 μm), while the lowest for extruding with fully open EFM.

4.4. Other factors that may influence mechanical performance

In general, the performance of PNC depends on several factors, e.g.:

1. Clay content;
2. Degree of dispersion (e.g., as expressed by d_{001} , N , and X_E);
3. Impurities and microstructure defects (solid particles, aggregates, or voids);
4. Crystallinity, e.g., crystalline content, size of crystals, crystallographic form (α , β or γ);
5. Polymer and clay orientation and its distribution within the specimen;
6. Level of degradation of the organoclay intercalant, additives, and the polymer;
7. Degree of polymer disentanglement and crosslinking;
8. Clay attrition during compounding and processing.

From the above list, the first two may be eliminated as in this paper the only clay concentration discussed was 2-wt% of C15A, and the effects of the degree of clay dispersion were discussed. Of the remaining factors the impurities, the polymer disentanglement or crosslinking, clay attrition, and orientation have not been measured. Thus, only few comments can be made regarding the effects of crystallinity and degradation.

The PA-6 based PNC's show a wide range of degree of dispersion. Here the modulus and strength correlate well with the extent of exfoliation, thus in PA-6 systems the clay dispersion dominates the tensile behavior. However, other factors seem to control the NIRT behavior.

The PNC's with PP + PP-MA as the matrix showed much smaller effect of compounding variables on the clay dispersion. Furthermore, the data indicate that the Hoffmann elimination process causing re-aggregation of clay platelets, accompanied clay dispersion. For these PNC's only the tensile strength correlated with the degree of dispersion – other factors seem to control the modulus and NIRT behavior.

Dell'Anno in his thesis³⁰ showed that the tensile modulus of all his specimens (including PP, and PNC with different clay content) linearly increased with the crystallinity content: $X = 28$ to 46% , i.e., that the system rigidity was controlled by the matrix. However, in the PP-based PNC's discussed in this paper the crystallinity content varied but little: from $X = 41$ to 44% . Thus, the observed poor correlation between modulus and clay dispersion cannot be explained by the crystallinity content.

The degree of the matrix degradation during compounding may be estimated from the melt flow rate (MFR at 230°C , with 2.16 kg weight). Since PP is sensitive to oxidation, temperature, and mechanical stresses, degradation during compounding could be expected. According to Basell data sheet the MFR of Pro-fax PDC1274 is 12 dg/min, while that of the resin extruded at 180°C through SSE + EFM-3 or EFM-N with the smallest gap of $15\text{ }\mu\text{m}$ gave the MFR = 11.94 (11.72 to 12.13) dg/min; hence well within the accepted error of measurements of ± 0.5 dg/min. Evidently, addition of organoclay and compatibilizing mixture of PP-MA's caused a decrease to MFR = 10.3 ± 0.2 in SSE alone or in SSE + EFM-3. The use of SSE + EFM-N increases the MFR to about 10.6 ± 0.2 dg/min, thus indicating only a small change at the most severe compounding conditions. Thus, the compounding line of SSE + EFM efficiently disperses the organoclay, but at the same time has quite benign effect on the polymeric matrix. Thus, the observed poor correlation between modulus and clay dispersion also cannot be explained by degradation.

5. Summary and conclusions

Melt compounding of PNC based on PA-6 or PP may be efficiently done using a simple extrusion line composed of SSE and EFM-N. For both systems, the XRD and TEM measurements indicated better dispersion of organoclay than that obtained using TSE, TSE + GP or TSE + GP + EFM. The degree of exfoliation increased with the reduction of EFM gap for PA and PP based PNCs. Full exfoliation of Cloisite® 15A in PA-6 matrix was obtained from SSE + EFM-N, but only partial from SSE + EFM-3. In short, better dispersion was obtained using SSE instead of TSE as the basic extruder, as well as better dispersion was achieved using the redesigned EFM-N instead of the commercial blending unit, EFM-3.

The reason for better performance of the SSE + EFM compounder than that of TSE + GP + EFM is not obvious. Dennis *et al.* [2001]³¹ reported that the best correlation between their “degrees of dispersion, DD” was with the residence time and its distribution. They also observed that better dispersion was obtained under not too severe compounding conditions. As shown in Table 2, at the same throughput the residence time in SSE + EFM is longer than that in TSE + GP + EFM. Furthermore, the former compounding line generates milder stresses than the second one, thus confirming the observation by Dennis *et al.* However, the whole story is a bit more complex, as the presence of properly designed EFM-N with small gap is necessary to generate good dispersion and high performance.

Good correlation between the degree of clay dispersion and mechanical properties was established for the PA-6 based PNC, viz. between tensile modulus and interlayer spacing, similarly between the tensile strength and degree of exfoliation. The impact strength was found to decrease when the PNC stiffness increased. However, different dependence was obtained for specimens compounded in TSE than for these compounded in SSE or prepared by reactive method – the origin of the disparity of results from these two compounding lines has not been identified.

In the PP based PNC the tensile strength demonstrated high degree of correlation with the clay dispersion but correlation was poor for the tensile modulus and impact strength. Evidently, the PNC performance is controlled not only by clay dispersion, but also by other factors as well.

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