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Melt Compounding of Different Grades Polystyrene With Organoclay. Part 3: Mechanical Properties

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We discuss the effects of the melt compounding variables, matrix molecular weight and organoclay content on the X-ray diffraction (XRD) and mechanical properties of polystyrene (PS)/organoclay nanocomposites (PNC) prepared in a twin-screw extruder. An increase of residence time reduced the height of the first XRD peak and increased that of the second peak. Barrel temperature and screw configuration had a little influence on the tensile properties and impact strength. Young's modulus increased with organoclay content and it was almost independent of matrix PS molecular weight. The stress-at-break and impact strength decreased with organoclay content and increased with PS molecular weight. Young's modulus and impact strength decreased with residence time. Since the slopes of these dependencies for PNC were similar to that of the neat PS, the matrix degradation seems to play the major role. The relationship between impact strength and elongation at break of PNC showed high dependency on matrix grade. However, better empirical correlation was observed between the impact and tensile strengths. According to theoretical model of Ji et al. [32], the Young's modulus vs. clay concentration dependence indicated the presence of low interphase thickness. POLYM. ENG. SCI., 45:827–837, 2005. © 2005 Society of Plastics Engineers

INTRODUCTION

One of the advantages of adding organoclay to a polymer matrix, i.e., making a polymer nanocomposite (PNC), is the

improvement of mechanical properties. For example, incorporation of 4.2 wt% of exfoliated montmorillonite into polyamide-6 (PA-6) increases the Young's modulus by a factor of 2.1 [1]. More recently, mechanical properties of PNC with polypropylene (PP) [2–4], polyamide-66 (PA-66) [5], polystyrene (PS) [6–8], etc., have been studied. Experimentally, when exfoliation is achieved, the Young's modulus of PNC with 4 wt% clay increases by a factor of approximately 1.5 to 2 over that of the neat matrix polymer [9]. However, such mechanical properties as tensile strength, elongation at break, or impact strength generally decrease with clay content. Of note, the modulus is calculated at the vanishingly low strains, whereas the other properties are determined at strains that correspond to yield or break, at which the stress transfer between matrix and reinforcing particles is important.

The early methods for the production of PNC were based on in-situ polymerization, i.e., an organoclay was dispersed in a monomer, which subsequently was polymerized. Current research focuses on the melt compounding process. For example, organoclay may be dispersed in a PA-6 matrix using either a twin-screw (TSE) or single-screw extruder (SSE) [10, 11]. Owing to the polar nature of PA-6, clay exfoliation, by melt compounding with suitable organoclay, is relatively easy. For example, a suitable organoclay for PA is Cloisite® 30B (montmorillonite [MMT] intercalated with methyl tallow di-2-hydroxy ethyl ammonium chloride) or SCPX-2004 (MMT with methyl rapeseed di-2-hydroxyethyl ammonium chloride). However, in the case of less polar polymers, melt compounding is difficult, requiring good thermal stability and often compatibilization. Thus, it is important to find the optimum conditions for PNC preparation by melt compounding.

Self-diffusion of polymer chains in the molten state is

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low, viz. the self-diffusion coefficient: $D_s = 10^{-10}$ to 10^{-16} m²/s, i.e., 1 min diffusion time results in the displacement ranging from 25 to 0.025 μ m, respectively [12]. Therefore, mechanical mixing is required for the effective preparation of PNC. TSE is the most common compounding system for this purpose. Considering the dynamics of twin screw extrusion, variables such as barrel temperature, screw speed, feed rate, and screw configuration are expected to affect the properties of the resulting PNC.

In the aforementioned studies [10, 11], the PNCs were prepared by compounding the resin with organoclay nanocomposites in a TSE or SSE, the former producing material with better performance characteristics. The authors observed that it was imperative to provide adequate residence time in the extruder and appropriate shear history. The degree of dispersion in the TSE correlated well with the mean residence time and dimensionless variance (which indicates residence time distribution), but not with the type of the machine or the stress field. Since the experiments were carried out at constant throughput, the results imply that strain is important for the preparation of PNC in a TSE. More recently, PA-6 based PNC were prepared in a TSE using water slurry of Na-MMT [13]. The properties of the product were nearly equal to those of conventional PNC.

Melt compounding has been successfully carried out using hydrophilic polymers as the matrix, viz. polyvinyl pyrrolidone, polyethylene glycol, and polyvinyl alcohol. There are some experimental studies suggesting the feasibility of the preparation of PNC from such polymers by melt compounding under selected process conditions, e.g., PP [14], poly[ethylene-co-(vinyl acetate)] (EVA) [15], PA-6 [13, 16], etc. However, systematic studies of melt compounding of PNC are scarce. A high degree of exfoliation was obtained by dispersing up to 9 wt% of Cloisite® 30B in a semiaromatic copolyamide [17] in a small TSE. Good results were also obtained using polycarbonate [18, 19] or epoxy [20]. Generally, it is quite difficult to exfoliate clay in low-polarity polymers, such as polystyrene [21, 22] or polyolefins [23].

The aim of this study was to provide a guideline for melt compounding of PS-based nanocomposites. In this article, we present the method used to melt-compound the PS-based PNC in a co-rotating TSE. Then, the effects of various processing conditions on the tensile and impact properties are presented, focusing on the interrelation between the extrusion conditions and mechanical properties. Cloisite® 10A and three grades of PS (with different molecular weight, M_w) were used. The effects of M_w of PS on mechanical properties of PNC are also discussed.

EXPERIMENTAL

Materials

Three PS grades were used. These are coded as LMW, MMW, and HMW, for low ($M_w = 230$ kg/mol), medium

($M_w = 270$ kg/mol), and high ($M_w = 310$ kg/mol) weight average molecular weight respectively [21, 22]. The organoclay (Cloisite® 10A) is a MMT (cation exchange capacity [CEC] = 0.926 meq/g, $d_{001} = 1.17$ nm) intercalated with 1.25 meq/g of di-methyl benzyl hydrogenated tallow ammonium chloride (2MBHTA), which increased the interlayer spacing to $d_{001} = 1.92$ nm.

Melt Compounding

As described in Part 1 of this series of articles [21], a Leistritz co-rotating twin-screw extruder TSE-34 (screw length/diameter ratio (L/D) = 40) was used. The residence time and its distribution inside the TSE were measured using an ultrasonic probe. The special die for in-line ultrasonic (US) monitoring was placed at the extruder exit. Detailed information regarding the equipment and procedures used in these measurements may be found elsewhere [24, 25].

In this study, the effects of: 1) PS grade; 2) organoclay content; 3) residence time; 4) barrel temperature (T_B); and 5) screw configuration on PNC's performance were examined (see Table 1). In Table 1, "Double pass" means that the PNC was first extruded by feeding PS from the hopper and the organoclay from the side feeder, and then the extrudates were loaded into hopper and reextruded under the same conditions as for the first pass (screw rotation, feed rate, barrel temperature, and screw configuration). Since PS is amorphous, the degree of clay dispersion is not affected by vitrification. Thus, the PNC may be remelted. Accordingly, "double pass" is equivalent to extrusion with a long residence time, calculated as the sum of residence times of organoclay during the first and second passes through TSE.

Normally, during the first (or single) pass, the organoclay was added from a side feeder. To test the influence of the feed mode, LS-2-5 specimen was extruded using a dry-blend of PS pellets and organoclay powder. As illustrated in Fig. 1, two types of screws were used, the high shear (HS) and low shear (LS) screws. The former screw had 30% and the latter screw 10% kneading and mixing elements.

X-ray Diffraction

X-ray diffraction (XRD) measurements were carried out using a Rigaku Rotaflex X-ray diffractometer with Cu-rotating anode and 2θ scan. XRD scans were obtained using an incident X-ray wavelength of $\lambda = 0.15406$ nm at a scan rate of $d\theta/dt = 1.5^\circ/\text{min}$. X-ray analysis was performed on the specimens prepared by compression molding at 200°C [21].

Mechanical Testing

Extruded PNC pellets were injection molded using a BOY-30A machine into standard tensile specimens (ASTM D638, Type I) and bars for Izod impact tests (ASTM D256). The barrel temperature was 200°C, mold temperature of 40°C, injection pressure of 18 MPa, a holding pressure of 7 MPa, and a cooling time of 20 s.

TABLE 1. PS/organoclay mixtures prepared by melt compounding.*

Sample code	Screw	T_B (°C) ^a	$Q(\text{PS})^b$ (kg/h)	$Q(\text{C10A})^c$ (kg/h)	Double pass	Mean residence time ^d $\bar{t}$ (s), single/double
HS-0-5	HS	180 or 200	5	0	Yes	—
HS-1-5	HS	200	5	0.05		169/—
HS-2-5	HS	180 or 200	5	0.1	Yes	169/406
HS-5-5	HS	180 or 200	5	0.25	Yes	169/406
HS-10-5	HS	200	5	0.5		169/—
HS-0-10	HS	200	10	0	Yes	—
HS-2-10	HS	200	10	0.2	Yes	96.1/229
HS-5-10	HS	200	10	0.5	Yes	96.1/229
HS-0-20	HS	200	20	0	Yes	—
HS-2-20	HS	200	20	0.4	Yes	62.7/148
HS-5-20	HS	200	20	1.0	Yes	62.7/148
LS-0-5	LS	180 or 200	5	0		—
LS-2-5	LS	180 or 200	5	0.1		Not measured
LS-5-5	LS	180 or 200	5	0.25		Not measured

*Common conditions: Screw rotation speed was $N = 200$ rpm. Double pass was done at barrel temperature of 200°C.

^a T_B is barrel temperature.

^b $Q(\text{PS})$ is PS feed rate in the hopper.

^c $Q(\text{C10A})$ is feed rate of Cloisite® 10A using side feeder.

^dOrganoclay residence time as measured by ultrasonic.

Tensile tests were carried out according to ASTM D638 using an Instron 5500R model 1125 tester. Crosshead speed was set up at 5 mm/min. An extensometer was used to accurately measure the strain. Young's modulus was calculated by least square formfitting of the experimental data of stress vs. strain in the initial region of strain from 0 to 0.2%.

Notched Izod impact tests (procedure ASTM D256) were performed at room temperature using an Instron Model 8200 impact tester. Property values reported here represent an average of 10 tests for each specimen. Before the tensile or impact tests, the specimens were dried under vacuum at 60°C for at least 48 h.

RESULTS

Residence Time Distribution

The residence time distribution was measured at screw rotation speed of $N = 200$ rpm, $T_B = 200^\circ\text{C}$ by means of an ultrasonic probe at frequency $\nu = 5$ MHz. CaCO_3 was used as the ultrasonic tracer. As shown in Part 1 [21], the resi-

dence time distribution curves for the three PS grades were quite similar—the peak position moved very slightly to shorter times as the M_w of PS increased. Otherwise, the curves virtually superimposed. Since the test results were insensitive to the melt flow properties, these measurements were carried out using neat MMW PS. The residence time distribution vs. feed rate was determined (see Fig. 2 and Table 1). The data can be approximated by a simple hyperbolic relation of the main feed rate, Q :

$$\bar{t} = a_0 + a_1/Q. \quad (1)$$

The effect of residence time, $\bar{t} = 62.7$ to 406 s, on the degree of clay dispersion (as evidenced by the XRD scans) is displayed in Fig. 3, while that on the mechanical behavior is presented in Fig. 4.

TSE Barrel Temperature and Screw Configuration

The effect of the screw configuration and the barrel temperature on the degree of dispersion, as indicated by

FIG. 1. TSE screw design and the location of side feeder. a: High shear type screw (HS). b: Low shear type screw (LS).

FIG. 2. Residence time distribution in a TSE with high shear type screw at three feed rates. Screw rotation speed was $N = 200$ rpm and barrel temperature 200°C .

XRD, is illustrated in Fig. 5. Note the similarity between scans for LS- 180°C , LS- 200°C and HS- 180°C .

Figure 6 displays the tensile properties and impact strength for the PNC specimens containing 0, 2, or 5 wt% organoclay, compounded at constant feed rate of $Q = 5$ kg/h at $T_B = 180$ or 200°C using either LS or HS screw configuration (see Table 1). There is large experimental variability in these measurements. Thus, only the global tendency is important.

PS grade and organoclay content

The influence of PS grade and organoclay content on the mechanical properties is illustrated in Fig. 7 (for XRD-curves, see Part 1 [21]). By contrast with other properties, the Young's modulus is almost independent of molecular weight of the PS. Its dependence on organoclay content can be approximated (correlation coefficient $r = 0.988$) by a linear equation:

$$E_c = 3.4 + 0.0631w \quad (2)$$

FIG. 3. X-ray diffraction results for MMW PS with 5 wt% organoclay extruded using high-shear screw at 200°C (HS-5-5, HS-5-10, and HS-5-20). The residence time varied from (bottom) 62.7 to 406 s (top).

where E_c is Young's modulus of composite and w is organoclay content.

DISCUSSION

Effect of Residence Time

Figure 2 displays the distribution of residence time at $T_B = 200^\circ\text{C}$ and $N = 200$ rpm for three feed rates at the TSE hopper. As indicated, Fig. 2a displays the distribution curves for tracer added from the side feeder, whereas Fig. 2b for tracer added from the hopper. These experimental data may be characterized by two parameters: the mean residence time, $\bar{t}$, and its normalized variance, σ^2 . Their numerical values were computed using the follow equations:

$$\bar{t} = \int_0^\infty tE(t) dt \quad (3)$$

$$\sigma^2 = \frac{\sigma_t^2}{\bar{t}^2} = \frac{\int_0^\infty (t - \bar{t})^2 E(t) dt}{\bar{t}^2} \quad (4)$$

where $E(t)$ is the residence time distribution. The computed values are listed in Table 2. Evidently, $\bar{t}$ and σ^2 decrease with the feed rate, Q . Noteworthy, the distribution curves are sharper for the tracer flow from the hopper to the exit (die) than those for feeding the tracer from the side feeder. Both these parameters, $\bar{t}$ and σ^2 follow the hyperbolic Eq. 1, with the parameters listed in Table 3.

As shown in Table 2, at the slowest feed rate, $Q = 5$ kg/h, the residence time $\bar{t} = 169$ or 237 s depends on whether the tracer flow is from the side feeder or from the

FIG. 4. Mechanical performance of MMW PS with 0, 2, and 5 wt% organoclay as a function of the residence time. Barrel temperature was $T_B = 200^\circ\text{C}$.

main hopper, respectively. For the “double pass” extrusions, the residence time was calculated as the sum of the residence time from side feeder to exit (first extrusion) plus that from hopper to exit of the TSE (second extrusion). The minimum and maximum residence times in this study were $\bar{t} = 62.7$ and 406 s, respectively.

The changes in XRD spectra caused by shearing PNC in the TSE within the full range of residence time are indicated in Fig. 3. For these tests, PS was compounded with 5 wt% organoclay at $T_B = 200^\circ\text{C}$ and $N = 200$ rpm. There are two peaks on each XRD curves. The first is located at $2\theta \approx 2.2$ to 2.3° and the second at $2\theta \approx 4.8$ to 5.3° . The interlayer spacing calculated from Bragg's formula is $d_{001} \approx 3.8$ to 4.0 and 1.7 to 1.8 nm, respectively [21]. Thus, the first peak indicates intercalation of Cloisite® 10A by PS macromolecules expanding the galleries (from the original value of $d_{001} = 1.92$ nm), while the second indicates the opposite effect. The first peak decreased in intensity with increasing residence time, while the second peak increased and its position also moved slightly to higher scattering angles, indicating progressive reduction of the interlamellar gallery heights. The origin of such a reduction was traced by Fourier Transform Infrared Spectroscopy (FTIR) spectra to the thermomechanical degradation of the intercalant [21].

Dennis et al. [10] demonstrated that it is not the intensity of the stress field in the TSE, but the residence time that is responsible for intercalation, as the intercalation and/or ex-

FIG. 5. X-ray diffraction results for PS/organoclay nanocomposites at $T_B = 180$ and 200°C , for high-shear (HS) and low-shear (LS) screws.

FIG. 6. Tensile properties and impact strength for PNC compounded in a TSE under the conditions listed in Table 1. Screw configuration is shown in Fig. 1.

foliation requires time. However, for the thermally unstable PS/Cloisite® 10A systems, the long residence time increases the effects of thermal degradation and causes reduction of spacing between the clay platelets, and thus reaggregation. The two processes, the time dependent intercalation and degradation, occur simultaneously. Detailed analysis of data indicates a local maximum of dispersion for residence time $\bar{t} \approx 100$ s, and worsening dispersion at longer residence times. Yoon et al. [19] reported similar behavior for the polycarbonate-based PNC.

Figure 4 displays the mechanical properties (Young's modulus, stress at break, elongation at break and impact strength) as functions of residence time for the nominal organoclay loadings of 0, 2, and 5 wt%. For PNC, the Young's modulus seems to reach a local maximum at residence time $\bar{t} \approx 100$ s, then it decreases. Stress and elon-

gation at break also decrease with residence time, reaching a plateau at long shearing times.

For all three compositions, the impact strength decreased with increase of residence time. The linear curve fitting of Young's modulus and impact strength data gave almost the same slope for all three compositions. Thus, deterioration of the PS matrix seems to be the main culprit for the reduced performance at longer residence times. The thermooxidative degradation of PS seems to be responsible for the loss of performance [21, 22].

Effect of Barrel Temperature and Screw Configuration

To study the effect of barrel temperature, T_B , and screw configuration on the organoclay dispersion and performance, MMW PS with 5 wt% organoclay was compounded

FIG. 7. Tensile and impact strength properties as a function of organoclay contents for three grades of PS.

in a TSE at a screw rotation speed of $N = 200$ rpm and feed rate of $Q = 5$ kg/h, at $T_B = 180$ or 200°C . The two screw configurations presented in Fig. 1, HS and LS, were used. Figure 5 displays the XRD spectra for the resulting specimens.

As in the case of Fig. 3, all the curves in Fig. 5 are characterized by the presence of two peaks. The first peak corresponds to short organoclay stacks with expanded interlayer spacings to about $d_{001} \approx 4$ nm, while the second corresponds to clay stacks with reduced interlayer spacing, viz. $d_{001} \approx 1.7$ nm. The relative population of these two clay types can be judged by the height of the corresponding peak. The first peak of the specimen extruded at $T_B = 200^\circ\text{C}$ using the HS screw is very small and the peak position of this specimen is located at the highest 2θ observed for the four cases. The three other spectra are similar, indicating an equivalence between the LS screw at $T_B = 180$ and 200°C and HS screw at $T_B = 180^\circ\text{C}$. The first peak position of the specimen extruded using the LS screw configuration is lower than for those extruded using the HS screw. Therefore, judging by the XRD data alone, the best dispersion of Cloisite® 10A in the PS matrix is obtained under the mildest compounding conditions using low shear

FIG. 8. Izod impact strength vs. elongation at break for various PS based organoclay nanocomposites. Barrel temperature of 200°C , screw rotation speed of 200 rpm, feed rate of 5 kg/h, and organoclay contents of from 0 to 10 wt%.

FIG. 9. Izod impact strength vs. tensile strength for PS-based PNC containing 0, 2, and 5 wt% organoclay, and prepared under different conditions.

(LS) screw configuration. These conditions seem to provide optimal balance between degradation and dispersion, under the conditions included in this study.

According to Fig. 6, the Young's modulus for specimens compounded using HS screws at $T_B = 200^\circ\text{C}$ is systematically higher than for those prepared at 180°C —this tendency is absent for the LS screw configuration. Since the trend is the same for the neat resin, evidently the temperature effect is unrelated to the degree of clay dispersion. Comparison between the LS and HS specimens indicates that marginally higher moduli (within the range of experimental error) are observed for the latter screw configuration.

Stress and elongation at break dependencies show similar tendencies. The best overall performance was obtained for LS screw configuration at $T_B = 200^\circ\text{C}$. For HS screw configuration compounding at $T_B = 180$ or 200°C gives the same (within the experimental error) values.

The effect of the compounding conditions on the impact strength is difficult to judge. For the same clay loading, the values are quite similar (within the error of measurement). The only clear tendency for this set of data (specimens prepared at $T_B = 180$ or 200°C using either LS or HS) is a systematic decrease of the impact strength with clay content. It has been frequently observed that the impact strength

TABLE 3. Feed rate dependence of the residence time distribution—see Eq. 1.

Parameter	Flow from	a_0	a_1	r
$\bar{t}$	Hopper	33.7	1013	0.9997
σ^2	Hopper	0.018	0.153	0.9953
$\bar{t}$	Side-feeder	26.3	712	0.9998
σ^2	Side-feeder	0.0571	0.0174	0.9858

shows the opposite tendency to Young's modulus. In particular, Vaia et al. [26] reported this behavior for PS-based nanocomposites. The data in Fig. 6 confirm these observations.

The viscosity of PS at 180°C is about 4 times larger than that at 200°C . Thus, at the same screw speed, if it is assumed that the melt temperature depends solely on the barrel temperature, the imposed shear stress on layered-clay at 180°C might be 4 times larger than that at 200°C . However, since the heat dissipation at HS is higher than that at LS, the advantage for compounding at $T_B = 180^\circ\text{C}$ may be compromised. Indeed, focusing exclusively on Fig. 6 data for this temperature (white rectangles in Fig. 6), better performance is observed for LS than that for HS screws. Since it is difficult for PS macromolecules to diffuse into the interlamellar galleries at low temperature, the observed advantage of compounding at $T_B = 180^\circ\text{C}$ using LS screws most likely originates from the optimized balance between shear dispersion of organoclay platelets and thermomechanical degradation. This explanation finds good support in the XRD data presented in Fig. 5.

Effects of Polymer Grade on Mechanical Properties

Figure 7 displays the mechanical test results (Young's modulus, tensile strength at break, elongation at break and impact strength) vs. organoclay content for the three PS grades. Young's modulus increases with organoclay content almost independently of the PS molecular weight. The data (see Eq. 2) suggest low aspect ratio, $p \approx 28$, for the organoclay stacks [9]. It is worth noting that similar calculations for well-exfoliated PNC based on PA-6 give $p \approx 200$. Owing to PA-6 matrix crystallization the latter value was slightly smaller than the value calculated from melt flow data $p \approx 287 \pm 9$. In short, the 10-fold smaller aspect ratio of organoclay than what might be expected for exfo-

TABLE 2. Residence time at different feed rate for screw speed of $N = 200$ rpm and temperature $T_B = 200^\circ\text{C}$.

Experiment code	Hopper feed rate, Q (kg/h)	Measurement region	Mean residence time, $\bar{t}$ (s)	Normalized variance, σ^2
HS-0-5	5	Side feeder $\rightarrow$ exit	169	0.0605
	5	Hopper $\rightarrow$ exit	237	0.0494
HS-0-10	10	Side feeder $\rightarrow$ exit	96.1	0.0591
	10	Hopper $\rightarrow$ exit	133	0.0324
HS-0-20	20	Side feeder $\rightarrow$ exit	62.7	0.0578
	20	Hopper $\rightarrow$ exit	85.8	0.0269

liated PNC in the PS matrix, indicates the presence of short stacks. In Part 1 [21], the broadening of the XRD peaks suggested the presence of stacks of about 4 clay platelets in PNC containing 5 wt% organoclay. Thus, the aspect ratio based on Young's modulus points toward a bulk-average interlayer spacing (under both XRD peaks) of $\bar{d}_{001} \approx 2.0$ nm.

Fornes et al. [27] also reported insensitivity of the Young's modulus to the matrix molecular weight. The authors studied PNC based on PA-6, compounded with organoclay prepared by reacting sodium-MMT with 2-hydroxyethyl methyl rapeseed quaternary ammonium chloride. Changing the number-average molecular weight from $M_n = 16.4$ to 29.2 kg/mol resulted only in a small change of the PNC modulus.

As shown in Fig. 7, the stress at break increases with PS molecular weight and it decreases with organoclay content. Its relative value (ratio of PNC stress at break to that of neat PS) is nearly independent of PS grade. By contrast, elongation at break shows the most dramatic decrease with clay content for PNC based on HMW, more moderate for the MMW and the smallest for LMW. Thus, the relative values for the three matrices would show different behavior. For organoclay content exceeding about 6 wt%, the PNC elongation at break is nearly the same for the three PS resins.

Figure 7 shows that Izod impact strength decreases with organoclay content for each PNC series. As in the case of stress at break, the profiles are parallel. Thus, the relative impact strength is nearly independent of PS grade. However, for HMW, MMW, and LMW series, incorporation of 10 wt% organoclay reduces the impact strength of the matrix by about 20, 30, and 45%, respectively. These decreases are significantly smaller than the 87% reported for PS compounded with 10 wt% of three different types of organoclay [7].

Yoon et al. [18] observed that the impact strength of PC based PNC is proportional to the elongation at break and this relationship is almost independent of the organoclay type. Since both PC and PS are amorphous, it was tempting to see whether this relationship is valid for the PNC specimens discussed in this article; Fig. 8 shows these results. The specimens under consideration were prepared under the same conditions, e.g., barrel temperature, feeding rate, screw configuration, screw rotation speed, etc. The dependence is not universal, but within each matrix grade there is a high degree of correlation: $r \geq 0.92$. The slopes decrease with M_w of PS. Similar tendency was reported for PC/clay nanocomposites [18].

Better empirical correlation was observed between the impact and tensile strengths. Figure 9 shows this relationship for MMW PS-based PNC prepared under various processing conditions, viz. feed rate, screw configurations, barrel temperatures, and organoclay content. The correlation coefficient of linear fitting curve is $r = 0.933$. The dependence is nearly independent of the matrix grade.

Theoretical Analysis of Young's Modulus

Several theoretical models have been proposed for Young's modulus of polymer/clay nanocomposites. Depending on the original model, these can be assigned to Halpin and Tsai [28] type or Takayanagi et al. [29] type. The difference between these two types is quite significant. The Halpin and Tsai [28] equations were originally derived for continuous fiber composites, while Takayanagi et al. [29] focused on a more general case of two-phase systems with diverse morphology. For example, Brune and Bicerano [30], as well as Hui and Shia [31] started with a simplified the Halpin and Tsai [28] theory in their derivation of PNC tensile modulus relationships. However, since the Halpin and Tsai [28] approach is valid for an idealized, well-oriented systems with filler particles well bonded to the matrix, the new relations may not be fully applicable to PNC with randomly oriented platelets imperfectly bonded to the matrix.

Ji et al. [32] adopted the Takayanagi et al. [29] two-phase model, expanding it into three phases: matrix, interphase, and filler particles randomly distributed in the matrix. These may be of any shape, viz. spherical, cylindrical, or lamellar. The model is fully general, with the three phases connected to each other in parallel and in series. As a consequence, there are two types of interphases, connected to the other phases; one "in parallel" and the other "in series." In the case of PNC, these may be treated as the interphase inside the stack of clay platelets, and that between the stacks and the matrix. For plate-like filler particles, having thickness t_c , and both length and width $= \xi_c$ (with, $\xi_c \gg t_c$), the Young's modulus may be expressed as:

$$\frac{1}{E_c} = \frac{1 - \alpha}{E_m} + \frac{\alpha - \beta}{(1 - \alpha)E_m + \alpha(k - 1)E_m / \ln k} + \frac{\beta}{(1 - \alpha)E_m + (\alpha - \beta)(k + 1)E_m / 2 + E_f \beta} \quad (5)$$

where $\alpha = \sqrt{[2(\tau/t_c) + 1]V_f}$; $\beta = \sqrt{V_f}$; E_c , E_m and E_f are Young's moduli of composite, matrix and filler, respectively, τ is the thickness of the interfacial region, V_f is the filler volume fraction and $k = E_i(0)/E_m$ is the ratio of the interphase modulus on the surface of a particle, $E_i(0)$, to that of the matrix, E_m . For PNC the controlling parameters are: the size of dispersed particles (t_c and ξ_c), thickness of the interfacial region τ , filler-to-matrix modulus ratio E_f/E_m , and the parameter k . The parameter k represents the ultimate modulus ratio of the interphase to matrix, assuming a linear gradient change in modulus between the matrix and the surface of particle – the value $k = 12$ has been arbitrarily chosen [32].

Equation 5 was applied to the experimental values of Young's modulus reported in this article. The following values of equation parameters were used: $E_f = 170$ GPa [33], $E_m = 3.4$ GPa, $t_c = 1$ nm [34], and $k = 12$ [32]. The volume fraction of clay in PNC was calculated assuming the

FIG. 10. Young's modulus vs. organoclay content for MMW-PS based PNC. Experimental values are shown as points, and the Ji et al. [32] model predictions as lines: solid and broken for the interface thickness of $\tau = 0.4$ and 2.0 nm, respectively. Other parameters are: $E_c = 170$ GPa, $E_m = 3.4$ GPa, $t_c = 1$ nm, and $k = 12$.

matrix polymer and clay density equal 1040 and 2860 kg/m³, respectively. Results of the computations are shown in Fig. 10 for a series of MMW-PS based PNC.

Experimental data are well described when introducing a thickness of the interphase $\tau = 0.4$ nm. This thickness is smaller than, e.g., $\tau = 7.0$ nm, calculated by Ji et al. [32] for PA-6 PNC. Although the parameters τ and k are both material constants, the role of k is not clear. For example, the assumption that $k = 12, 6$, and 2 results in $\tau = 0.4, 0.7$, and 2.0 nm, respectively. These values of τ are all smaller than those published for PA-6 PNC, indicating poor exfoliation of the PS-based PNC. Furthermore, the small thickness of the interphase may imply poor interactions between clay platelets and polymer matrix.

In short, the thickness of the interphase cannot be quantitatively determined from the Ji et al. [32] model. The modulus of the organic phase adsorbed on the high-energy surface of crystalline MMT platelet is known [35] to be high, but value of the ratio k may vary with the system. However, this model provides the correct tendency of the interphase contribution.

CONCLUSION

PS based nanocomposites with commercial organoclay were prepared by melt compounding in a TSE. In this third part, we discuss the effects of the melt compounding variables as well as the matrix resin molecular weight and organoclay content on the mechanical performance of produced PNC.

Optimum PNC performance results from two competing processes: the shear dispersion of organoclay platelets and the thermomechanical degradation of the intercalant. Barrel temperature and screw configuration had a little influence

on the tensile properties and impact strength. According to the overall experimental results, milder compounding conditions (low-shear screw configuration and lower barrel temperature; 180°C in this study) provided marginally better performance than the high-shear screw.

An increase of residence time reduced the height of the first XRD peak and increased that of the second peak. Long compounding time reduced the degree of clay dispersion and mechanical performance. Adjusting the residence time in the extruder optimized the mechanical properties. However, owing to the thermomechanical degradation effects varying the compounding conditions resulted in relatively minor overall improvement of the PNC performance.

Young's modulus increased with organoclay content, almost independently of the matrix molecular weight. The stress at break and impact strength decreased with organoclay content and increased with PS molecular weight. Their relative parameter values (i.e., PNC parameter divided by that of the matrix) showed similar dependence.

Young's modulus and impact strength decreased with residence time. Similar tendencies were observed for other tensile properties. Since the slopes of these dependencies for PNC are similar to that of the neat PS, the matrix degradation seems to play the major role.

Relationship between impact strength and elongation at break of PNC, prepared under same compounding conditions, showed strong dependence on matrix grade. However, better empirical correlation was observed between the impact and tensile strengths.

The Young's modulus vs. organoclay content dependence was analyzed using the multiphase model, recently proposed by Ji et al. [32]. Fitting the experimental data to the model predictions indicated narrow interphase thickness, $\tau = 0.4$ nm, i.e., approximately 17.5 times smaller than that calculated for PA-6 PNC. The thin interphase indicates poor exfoliation in the PS-based PNC, and weak interactions between clay and the PS matrix.

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NOMENCLATURE

a_0	Constant of Eq. 1
a_1	Constant of Eq. 1
D	Screw diameter (mm)
d_{001}	Interlayer spacing of clay (nm)

$\bar{d}_{001}$	Bulk-average interlayer spacing (nm)
$E(t)$	Residence time distribution
E_c	Young's modulus of composite (GPa)
$E_i(0)$	Interphase modulus on the surface of a particle (GPa)
E_f	Young's modulus of filler (GPa)
E_m	Young's modulus of matrix (GPa)
k	Ratio of the interphase modulus on the surface of a particle to that of the matrix
L	Screw length (mm)
M_n	Number average molecular weight
M_w	Weight average molecular weight
N	Screw rotation speed (rpm)
p	Aspect ratio of a clay platelet
Q	Feed rate (kg/h)
r	Correlation coefficient
t	Time (s)
$\bar{t}$	Mean residence time (s)
t_c	Thickness of plate-like filler particles (nm)
T_B	Barrel temperature (°C)
V_f	Filler volume fraction
w	Organoclay content (wt%)
θ	X-ray diffraction angle (deg)
λ	Wavelength of X-ray radiation (nm)
ν	Frequency of ultrasonic (MHz)
ξ_c	Length or width of plate-like filler particles (nm)
σ^2	Normalized variance of the mean residence time
τ	Thickness of the interfacial region (nm)

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