

Mechanical Properties of Polystyrene-Montmorillonite Nanocomposites—Prepared by Melt Intercalation

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ABSTRACT: A series of polymer-clay nanocomposite (PCN) materials, consisting of thermoplastic polystyrene (PS) sample and dispersing inorganic organoclay platelets, were successfully prepared. First, organoclay was prepared by performing cationic exchange reactions between the sodium ions existing in the interlayer region of the clay mineral and intercalation agent, followed by dispersing the organophilic clay into a PS basis through the melt intercalation approach performed by a twin-screw mixing method. The as-prepared PCN materials in the form of a pellet subsequently characterized using the powder X-ray diffraction (XRD) and the transmission electron microscopy (TEM). In this study, it is found that the wear resistance of PS to be effectively enhanced by the incorporation of low loading organophilic clay platelets. The surface morphological image for the neat PS and PS-clay after a wear resistance test has also been compared and identified by the scanning

electron microscopy (SEM). Furthermore, the effect of organoclay on three other different measurement types of mechanical properties for as-prepared PCN materials, e.g., flexural tests, impact tests, and micron-nano indenter tests were performed and compared. Generally, PCN materials exhibited an obvious enhancement of mechanical properties of neat polymer by an incorporated low loading of organophilic clay platelets into a polystyrene matrix used for the evaluation of mechanical properties as-prepared samples. For example, mechanical strength (excepting flexural strength) almost remain same beyond 3 wt % clay loading in PS, whereas much detrimental effect being observed in the wear loss in case of PCNs with 5 wt % clay than 3 wt %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 288–296, 2010

Key words: polystyrene; clay; nanocomposite; melt intercalation; mechanical property

INTRODUCTION

Polystyrene (PS) is an engineering thermoplastic vinyl polymer, produced typically by free radical vinyl polymerization from the monomer styrene. PS is one of the popular commercial polymers, because of its unique properties, including excellent electric insulation, thermal insulation, and good chemical resistance properties. Currently, PS is widely used in computer, architecture, automotive, air, and railway transportation systems for tribological applications. However, major drawbacks in PSs applications are attributed to its poor native mechanical properties such as flexural, impact, and wear resistance. It should be particularly noted that the mechanical strength of polymers is the fundamental property needed to be fulfilled before they can exhibit their major useful service properties.

Lately, layered materials, such as smectite clay (e.g., montmorillonite, MMT) have attracted intense research interests for the preparation of polymer-clay nanocomposite (PCN) materials. PCN materials usually exhibit unique properties superior to traditional composites and conventional materials. Generally, they combine both the characteristics of inorganic nanofillers and organic polymers at the molecular level. Currently, the PCN material is found to be a promising system due to the fact that the clay possesses a high aspect ratio and a platy morphology. It can be used to boost the physical properties (e.g., thermal stability,¹ fire retardant,² gas barrier,³ and corrosion protection^{4–15}) of bulk polymers, mechanical properties is a particularly significant issue to study application and development for PCN materials. Kim and White¹⁶ reported a variety of organic modified MMTs to understand the contribution of the organophilicity of organoclay on the formation of the polymer/clay nanocomposite.

Several attempts to prepare PS-clay nanocomposite materials have been reported. For example, Kato et al.¹⁷ reported that the intercalation of PS in stearyltrimethyl-ammonium cation exchanged montmorillonite (MMT) by an *in situ* polymerization. Akelah and Moet^{18,19} prepared polystyrene nanocomposites

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using acetonitrile as a solvent. Doh and Cho²⁰ reported the synthesis of intercalated polystyrene-MMT nanocomposites by *in situ* polymerization of styrene containing dispersed organophilic MMT.^{21–23}

Recently, several attempts have been reported to study the mechanical properties of PS–clay nanocomposite materials.²⁴ For example, several research groups have reported the impact strength of PS–clay nanocomposite materials. On the other hand, flexible strength of PS–clay nanocomposite materials has also been reported. Moreover, wear resistance of PET and nylon 66 nanocomposite materials has been reported by Schadler and coworkers²⁵ and Yu et al.²⁶ However, wear resistance of PS–clay nanocomposite materials have seldom been mentioned.

Therefore, in this article, we present the first evaluation of wear resistance of PS–clay nanocomposite materials and are the first to make a comparative study on the mechanical properties of the effect of organoclay on flexural strength, impact strength, and microhardness of PS–clay nanocomposite materials.

EXPERIMENTAL

Chemicals and instrumentations

Commercial PS ($M_w = 350,000$, Aldrich, Model No. PG33) were purchased as pellets from the Qimei Stock Company in Taiwan. Hexadecyltrimethyl ammonium (HDMA) bromide (Sigma) was used as received without further purification. The montmorillonite clay (PK805), purchased from Pai-Kong Ceramic Company (Taiwan), was used and had a cationic exchange capacity (CEC) value of 98 meq/100 g.

A wide-angle X-ray diffraction study of the samples was performed on a Rigaku D/MAX-3C OD-2988N X-ray diffractometer with a copper target and Ni filter at a scanning rate of 4°/min. The samples for the transmission electron microscopy (TEM) study were first prepared by putting the membrane of PCN (PS–clay nanocomposite) materials into low-viscosity embedding media epoxy resin capsules with four ingredients (ERL4206 5.0 g, DER736 3.0 g, NSA 13.0 g, and DMAE 0.15 g) and by curing the epoxy resin at 100°C for 24 h in a vacuum oven. Then, the cured epoxy resin containing PCN materials were microtomed with a Reichert-Jung Ultracut-E into 60–90-nm slices. Subsequently, one layer of carbon about 10-nm was deposited on these slices on mesh 100 copper nets for TEM observations on a JEOL-200FX, with an acceleration voltage of 120 kV. Centrifugal Ball Mill (Retsch S100) was used to mill the size of organophilic clay. Twin-roll mill (Kobelco, model KXY-30) was used to meltmix the organoclay and PS. A plastograph-mix and a hot-press machine manufactured by Brabender Machine

Company (Germany, Model no. PLE-331, corotating type, nonintermeshing, Max screw speed is 120 rpm, L/D ratio is 32, test temperature is 20–400° C, chamber maximum volume is 50 g) and Long-Chang Company (Taiwan, Model no. FC-60 TON) were used to make the as-prepared sample in the form of an ASTM D3039 standard shape.

The flexural test of PCN membranes was performed through a Universal testing instrument manufactured by Hung-Ta Company (Taiwan, Model no. HT-9102). The impact strength test of PCN membranes was performed through an Izod Impact Tester manufactured by Hung-Ta Company (Taiwan, Model no. HT-8041B). The micron-nano hardness tests were run on an Ultra-Micro Indentation tester by CSIRO Company (Model UMIS2) for high and low hardness samples and an indentation time of 10 s at 25° C. The wearing resistance tests were run on a wearing test machine by the TABER Company (Model 5130 ABRASER).

Preparation of organophilic clay

The organoclay was prepared by a cationic exchange reaction between the sodium cations of MMT clay and quaternary alkylammonium cations of intercalating agent. The equation for calculating the intercalating agent used for cationic exchange reaction was as follows:

$$\begin{aligned} &98/100 \times 5 \text{ g (for clay)} \times 1.2 \\ &= (X/M_w \text{ of intercalating agent}) \times 1 \times 1000 \end{aligned}$$

where X represented the amount of used intercalating agent, 98/100 represents the cationic exchange capacity (CEC) value per 100 g of MMT clay, 1.2 (>1) indicating an excess amount of intercalating agent was used. Typically, 30 g of MMT clay with a CEC value of 98 meq/100 g was stirred overnight in 1000-mL distilled water (Beaker A) at room temperature. A separate solution containing an excess amount of intercalating agent (12.8 g) in another 200 ml of distilled water (Beaker B) was stirred for 1 h using a magnetic stirrer, followed by adding a 1M HCl aqueous solution to adjust the pH value to about 3–4. After stirring for 1 h, the protonated amino acid solution (Beaker B) was added at a rate of approximately 10 ml/min, with vigorous stirring, to the MMT suspension (Beaker A). The mixture was stirred overnight at room temperature. The organoclay was recovered by filtering the solution in a Buchner funnel. Washing (use water) and filtering the samples repeatedly for at least three times to remove any excess of ammonium ions showed the purification of products.

Preparation of PS–clay nanocomposite materials by melt intercalation

The as-prepared organoclay was first milled by a centrifugal Ball Mill machine (S-100) and followed by mixing and melting the as-prepared organoclay at 200°C using a twin-roll mill for 15 min under a dynamic vacuum at room temperature. Before blending the PS, the clay were dried at 90°C under a vacuum oven for 1 h. PS-clay composites were prepared in a Plastograph-Mixer machine twin-screw extrude at 210°C. First, at a screw speed of 65 rpm to blend for 6 min, 75 rpm to blend for 4 min, as a total the blending times were 10 min.

Hot press of PS–clay composite materials

According to the test standard of the experiment project, we designed the mold for the hot-pressing requirement, and then used the hot-press machine to undergo our tests. Place the mold under 210°C and pressure of 150 kg/cm². Hold the pressure for 3 min and let the pressure leak out for 30 s. Repeat this test three times, and then take the mold out after the hot press is finished. Last, wait for the mold to cool down to room temperature, then open the mold to take out the specimen.

Test of bulk mechanical properties

Flexural strength test

A flexural test can measure the deformation energy or fracture strength that bears the bending moment for determining materials. In general, there are three kinds of measurement methods of flexural tests: cantilever, three points, and four points. It is common to use the three points to measure in laboratories. Its method is to put the test specimen on two fixed displacements, apply force at the central point, with a certain pressing speed, until the test specimen fractures. It can use the flexural test to determine Young's modulus. Also, the experiment is done according to the ASTM D790 standard.

Impact strength test

The impact test is used to exert impact power to the specimen and to break the material by the impact of the external force. It can determine the energy absorbed by the broken specimen and show the impact value of a material. So, whether a brittle or ductile material can be compared by impact strength. This experiment was used in an Izod testing machine and made the specimens according to the ASTM D256 standard. Before the test we made a notch on the example specimen, and used a hammer to break up the specimen.

Test of surface mechanical properties

Micron-nano indenter test

We used the Australia UMIS Nano Indenter as the depth-detect instrument that our nano hardness test was carried on, and the selection the triangular awl modeling (Berkovich) for investigation. Because of the detection equipment's accuracy and sensitivity for micro-nano hardness tests, the temperature and humidity of the environment is controlled, and anti-vibration is also considered. We will hold the hardness measuring apparatus and use the ceramic board to be heated on the appearance first, then put thermal glue on inserting hold base, keep the experiment specimen parallel to the horizontal plane, to ensure that the examination is in the vertical accuracy of the moving direction (*z* direction). Then micronano hardness measurements can be performed after the inserting hold cools down. Also, the experiment is done according to the IEC 61010-1 & EN 61010 standard.

Wear-resistance test

The wear-resistance test is one of the most convenient and basic properties of material in mechanical properties testing. When one object is being used and is in contact with other objects for a long time, it will cause wearing. So, it's necessary to perform a long period of wearing-tearing test. This experiment uses wearing-test machines to determine the material's roll wearing and slip wearing, then show this material's surface decreasing ability on wear resisting. Also, the experiment is done according to the ASTM D4060 standard.

RESULTS AND DISCUSSION

In our previous study, hexadecyltrimethylammonium (HDMA) bromide-modified organoclay was found to display the highest value of *d* spacing at ~20 Å²⁷ and therefore was chosen to be used in the subsequent studies associated with the melt intercalation of polymers. The composition of the PS–clay nanocomposite materials varied from 0–5 wt % of organoclay to the PS content are summarized in Table I.

Characterization

Figure 1(a,b) showed the wide-angle powder XRD patterns of raw clay (Na⁺–MMT clay), organoclay (CTAB clay), and series of PCN materials. For PsCN1, there is any diffraction peak in 2 Θ = 4.9° (*d* spacing = 9 nm), as opposed to the diffraction peak of 2 Θ = 4.5° (*d* spacing = 1.96 nm) for organoclay, indicating the possibility of having exfoliated silicate nanolayers of organoclay dispersed in the PS

TABLE I
Relations of Composition of PS-clay Nanocomposite Materials Prepared by Melt intercalation, with Mechanical Properties

Compound composition	Feed code (wt %)		Flexural strength (MPa)	Impact energy absorption (J)	Micronano hardness (Hv)	Wear loss (mg)	
	PS	MMT				500 rpm	1000 rpm
PS	100	0	9.25	8.8	18.38	71	120
PsCN0.5	99.5	0.5	9.69 (+4.8%)	8.63 (-1.9%)	19.89 (+8.2%)	-	-
PsCN1	99	1	10.10 (+9.3%)	8.14 (-7.6%)	21.53 (+17.1%)	61 (-14.1%)	106 (-11.7%)
PsCN2	98	2	10.87 (+17.6%)	7.80 (-11.3%)	22.58 (+22.8%)	-	-
PsCN3	97	3	11.76 (+27.2%)	7.14 (-18.8%)	23.88 (+29.9%)	52 (-26.8%)	101 (-15.8%)
PsCN5	95	5	12.62 (+36.5%)	6.98 (-20.7%)	24.13 (+31.3%)	153 (+115.5%)	272 (+126.7%)

matrix. With the amount of organoclay increased to 3 wt %, there is a small peak at $2\Theta = 4.84^\circ$, corresponding to a d spacing of 9.12 nm. This implied that there was a small amount of organoclay that couldn't be exfoliated in the PS and existed in the form of an intercalated layer structure.

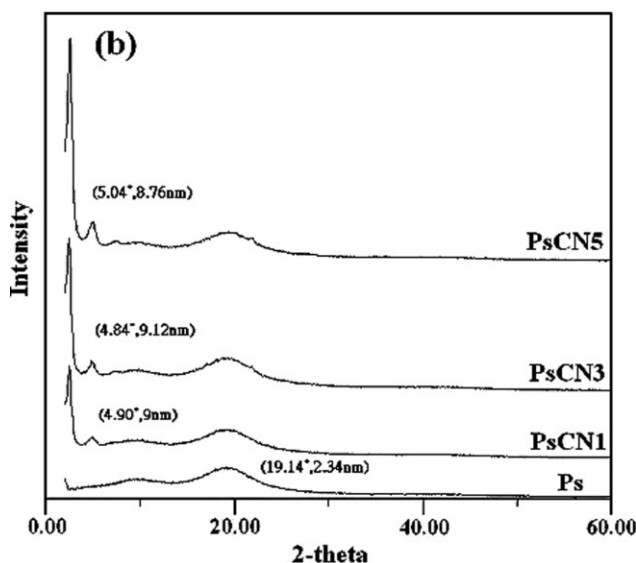
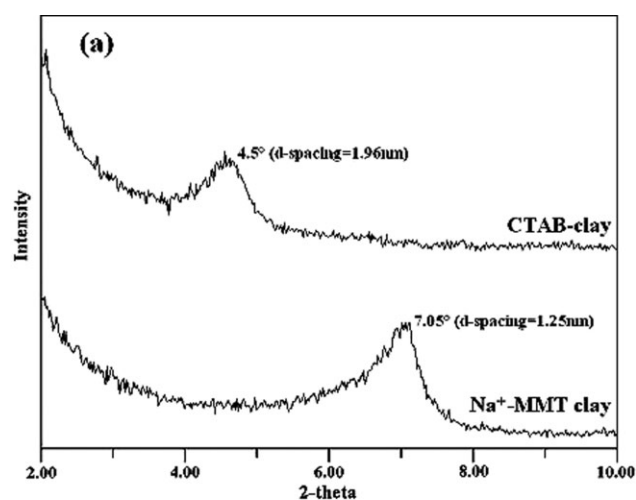


Figure 1 (a) X-ray diffraction patterns of Na^+ -MMT clay and CTAB clay. (b) X-ray diffraction patterns of neat Ps and Ps-MMT clay.

Figure 2 showed the TEM image of organophilic clay (MMT). As shown, organophilic clay is mostly regarded as one or more layers of the unit aggregate and forms the island's structure. This result shows that it has a partial property of nanocomposite materials.

Regarding the microstructure, the clay particles are dispersed in the polymer matrix in either intercalated or exfoliated states. Intercalated nanocomposites are in general obtained when the polymer is located between the silicate layers; even though the layer spacing increase, there are still attractive forces between the silicate layers to stack the layers in uniform spacing. Exfoliated nanocomposites are formed when the layer spacing increases to the point where

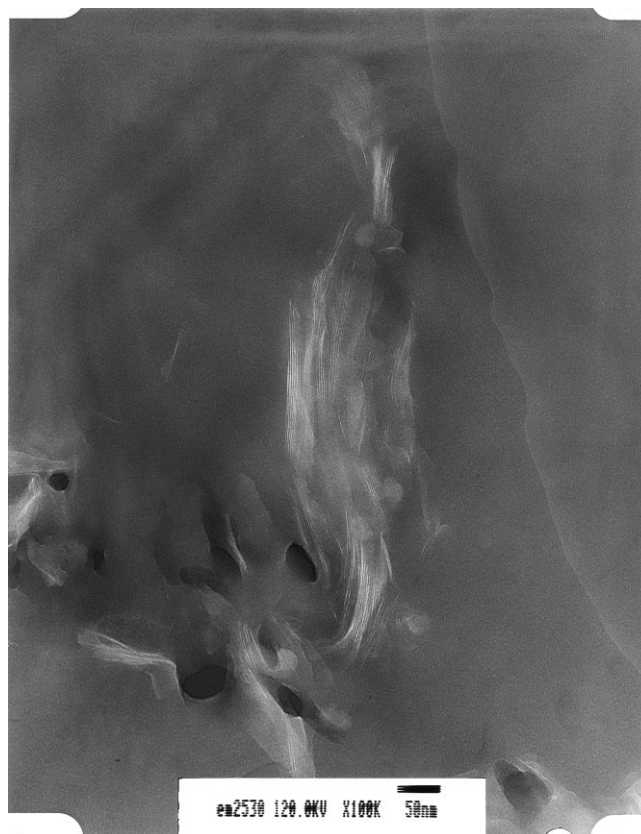


Figure 2 TEM image of organoclay (MMT) ($\times 100$ k).

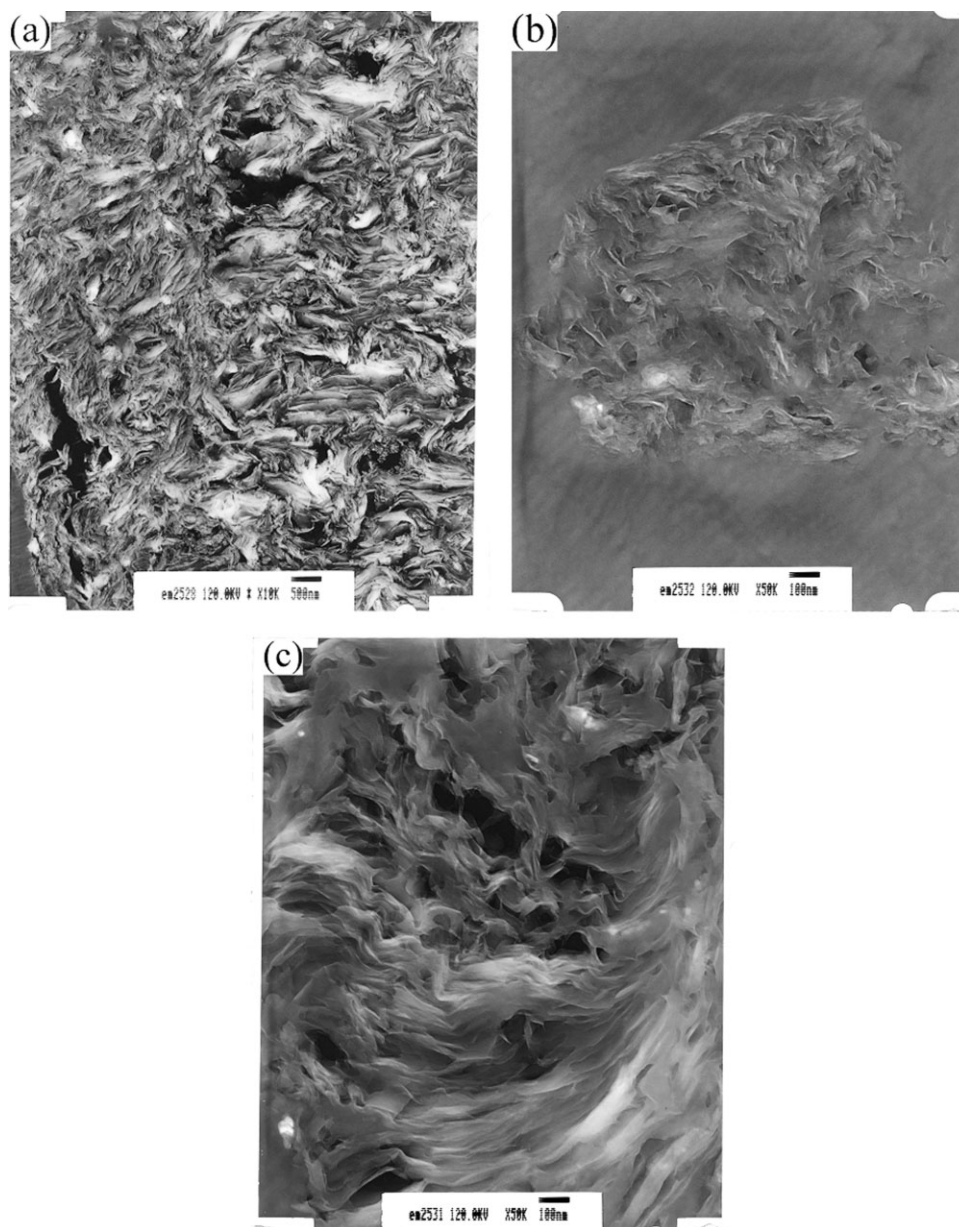


Figure 3 TEM images of PsCN5 (a) at $\times 10$ k magnification and (b,c) at $\times 50$ k magnification.

there are no longer sufficient attractions between the silicate layers to maintain an uniform layer spacing.²⁸

In addition to the XRD investigation, the internal structure of polymer/clay nanocomposites was also examined using TEM, which can directly visualize the expanded layering structure in the nanocomposites and the dispersion quality of the silicate layers in the polymer matrix.²⁹

Figure 3 showed the TEM micrograph of PCN materials loaded with 5 wt % clay, where the dark line represents clay platelets and the gray/white areas represented the PS matrix. Figure 3(a) is a lower magnification micrograph showing a general view of the dispersed clay particles in the PS matrix. Figure 3(b,c) is a higher magnification micrograph revealing

the d spacing of the clay layers in the PS matrix. It is clearly seen that lamellar nanocomposites has a mixed morphology with major intercalation and minor exfoliation dispersion in the PS matrix. Some larger intercalated tactoids could be identified with layer spacings of about 5 nm, as shown in Figure 3(b).

Bulk mechanical property studies

Flexural strength test

In this study, the relationship between flexural properties and organoclay loading as obtained from the flexural test on the standard shaped specimen (according to ASTM D790 standard) of PS-clay

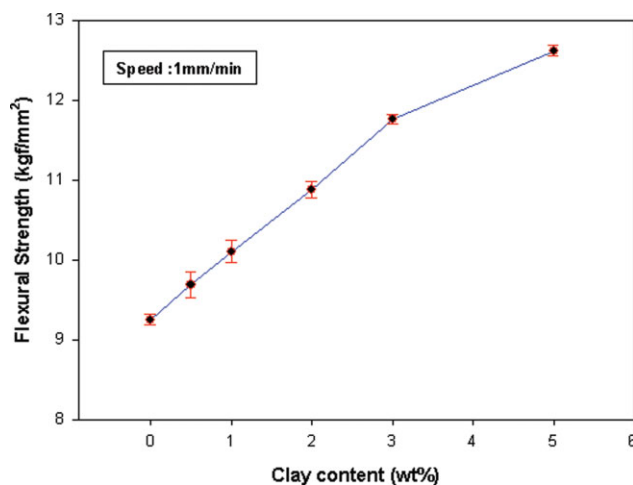


Figure 4 Variation of flexural strength of PsCNs nanocomposites with clay content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nanocomposite materials was studied, as shown in Figure 4 and Table I. For example, we found that the incorporation of organoclay platelets into a polymer matrix increased as the organoclay loading increased in the nanocomposites. For example, the neat PS has relatively low flexural strength (i.e., 9.25 kgf/mm²). On addition of organoclay into PS, the flexural strength increased obviously up to 9.69 kgf/mm² for PsCN0.5, to 10.10 kgf/mm² for PsCN1, to 10.87 kgf/mm² for PsCN2, to 11.76 kgf/mm² for PsCN3, and to 12.62 kgf/mm² for PsCN5. Thus, the flexural strength of the polymers can be improved significantly by the incorporation of organoclay platelets through melt intercalation approach and can be controlled by varying the organoclay content in the nanocomposite materials. Because the neat PS matrix is comparatively hard and brittle. Therefore, although the addition of organoclay into the matrix has already improved its bond strength, but the optimum organoclay content is a result of the formation of abrasive aggregates. If the organoclay content demonstrates better scattering in the PS matrix, the flexural strength of the polymers can be improved gradually (elevating at a steady rate). This finding can be further identified by the impact strength measurements of composites as discussed in the following sections.

Impact strength test

The impact strength test of as-prepared PCN materials was performed according to the ASTM D256. It should be noted that the impact energy absorption of the PS–clay nanocomposite materials were decreasing as the organoclay loading increased in the composite, as shown in Figure 5. The angle of the ham-

mer shock is increased from 142.9° to 143.3°. The higher the angle of the hammer strike, the smaller the impact on energy absorption, so the shock resistant intensity is found to be relatively worse because the neat PS matrix is comparatively hard and brittle. Therefore, although the addition of organoclay into the matrix has already improved, its bond strength and demonstrated better scattering in the matrix. However, an addition of organoclay still impelled the nanocomposite materials when struck by the external force caused a phenomenon of stress concentration. After that, the nanocomposite materials turned into the macroscopic stress fractured, resulting in reducing its already existing shock resistant characteristic. That is, to say if you add more organoclay; its shock resistant intensity becomes worse, so adding organoclay to shock resistant characteristics have not strengthened its function.

Surface mechanical property studies

Micron-nano indenter test

The micronano hardness is an important parameter for evaluating or designating nanocomposite materials. The hardness data of the PS–clay nanocomposite materials in the form of a standard shape at various material compositions are given in Figure 6 and Table I. The neat PS has relatively low hardness (i.e., 18.38 Hv). On addition of organoclay into PS, the hardness increased to 19.89 Hv for PsCN0.5, to 21.53 Hv for PsCN1, to 22.58 Hv for PsCN2, to 23.88 Hv for PsCN3, and to 24.13 Hv for PsCN 5. Thus, the hardness of the polymers can be improved significantly by the incorporation of organoclay platelets through melt intercalation approach and can be controlled by varying the organoclay content in

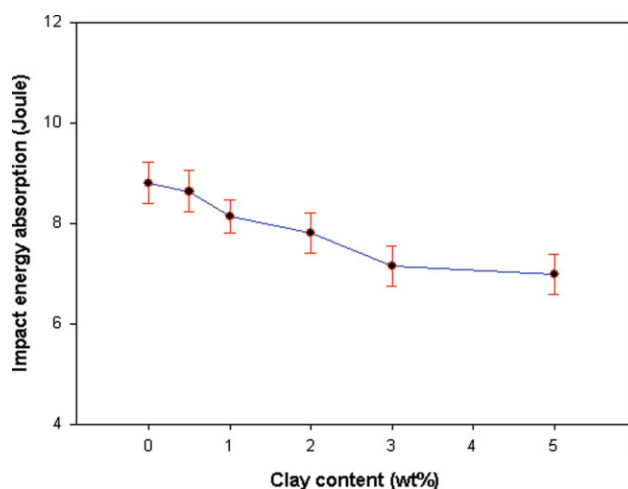


Figure 5 The impact energy absorption of PsCNs nanocomposites as a function of clay content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

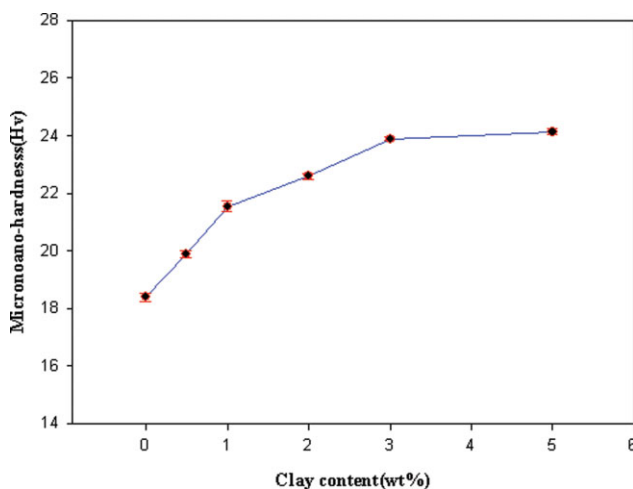


Figure 6 Effect of clay content on micronano hardness of PS/CNTs nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the nanocomposite materials. Figure 7 showed the micronano hardness indentation displacement of the PS-CNTs nanocomposites as a function of CNTs content. As shown, the indentation displacement of PS when the load begins to reach the greatest load and unloads finishing is the biggest displacement in an experiment, i.e., 6.2 μm , shows relatively poor hardness. Increasing CNTs content gradually and the indentation displacement in the trend moves left, namely reducing the displacement amount. Add 5 wt % to the CNTs content of the PS-CNTs nanocomposites and if displacement amount is small, the displacement amount is shortened from original 6.2–5 μm , showing that its hardness value is relatively high. Taught by the experiment here, adding organoclay contributes to improving the hardness of PS-CNTs nanocomposites. This can be further identified

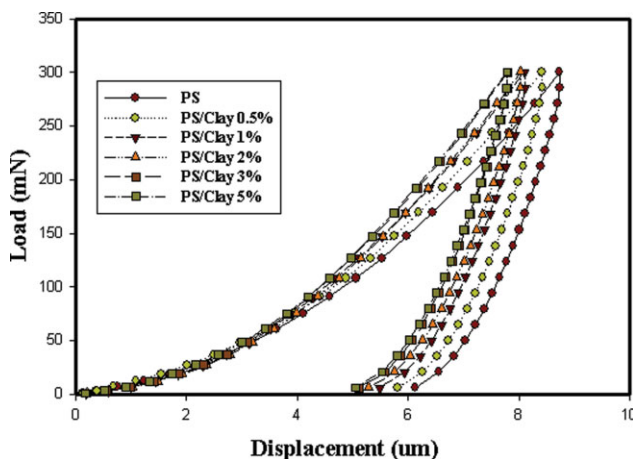


Figure 7 The load of PsCNTs nanocomposites as a function of micronano indentation displacement. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by the wear-resistance measurements of composites as discussed in the following sections.

Wear-resistance test

Figure 8 showed the wear mass loss versus organoclay loadings for PCNs nanocomposites. As shown, the wear circles were 500 and 1000 rpm. Wear mass loss decreased as the organoclay loading increased in the composite. The organoclay loading on 1–3 wt % shows this especially, the wear mass loss amount lessens gradually, improving from the original 71–52 mg for 500 rpm and 120 mg to 101 mg for 1000 rpm, showing that the consumed property of wear resisting has already been improved. It has been already known that wear mass loss (the influence factor of the wear mass loss amount) is the main impact factor in hardness of nanocomposite materials itself and heat conduction characteristic. Also, adding organoclay can make PCNs nanocomposite hardness improve. In the same way, it also improves the wear resisting property.

The wear mass loss amount increase at loading higher than 3 wt %, with the 5 wt % filled nanocomposite displaying the poorest properties. The phenomenon of optimum clay content has been observed for several systems. However, an explanation for why the wear of the nanocomposite increase beyond an optimum clay content is lacking. It is hypothesized that the phenomenon of optimum clay content is a result of the competitive effects of transfer film development and the formation of abrasive aggregates. Such aggregates are not seen on the wear surfaces indicating that the aggregates are formed in the transfer film due to continuous shear. With increasing filler loading, the ease of formation of these aggregates in the transfer film is enhanced

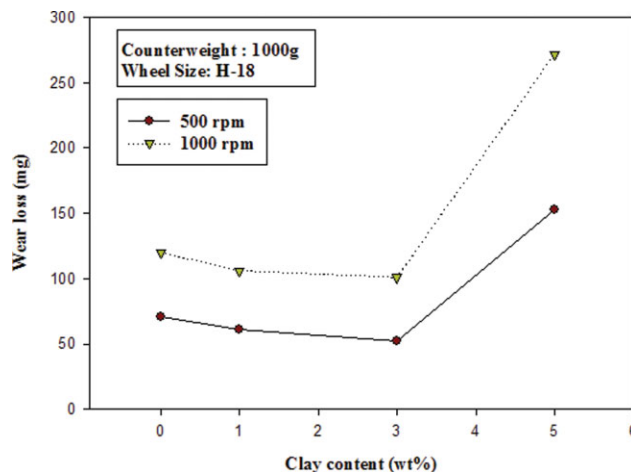


Figure 8 Wear loss versus organoclay loadings for PsCNTs nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

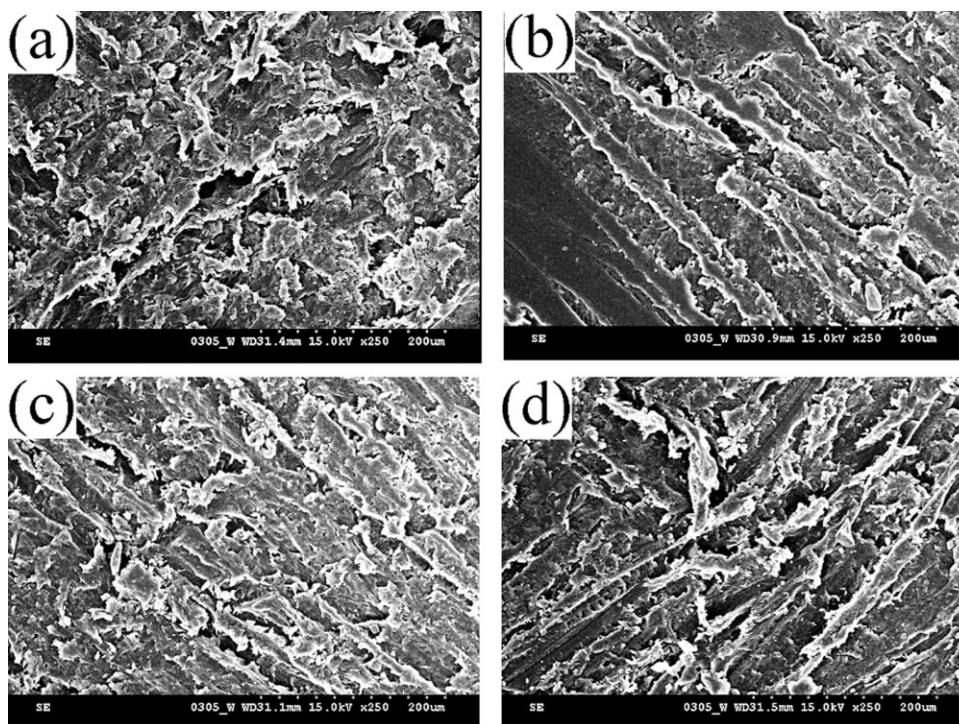


Figure 9 Wear SEM images of organoclay loadings for PsCNs nanocomposites at $\times 250$ magnification. Clay content (a) 0%, (b) 1%, (c) 3%, and (d) 5%.

due to the reduced interparticle distance in the parent sample.²⁵

Clay addition might contribute to increases in the local compressive and shear strength. Because the strengthening effect of clay with a weight percent of 5% as a reinforcing agent comes to the maximum, the changing tendency of the mechanical strength (excepting flexural strength) almost remain same beyond 3 wt % clay loading in PS, whereas much detrimental effect being observed in the wear loss in case of PCNs with 5 wt % clay than 3 wt %.

Moreover, the wear resistance of as-prepared composites can be further evaluated by the visual observation of the as-prepared composites after the wearing test. Figure 9 showed the scanning electron microscope (SEM) of neat PS (a), PsCN1 (b), PsCN3 (c), and PsCN5 (d).

It showed that the SEM observation of neat PS morphology revealed an uneven, rough surface indicating that the neat PS had soft surface structures. After the wearing test, the material structures of neat PS on testing can be easily degraded and removed from the surface of as-prepared sample, as shown in Figure 9(a). However, the surface morphology of PCN composites was found to display a relatively smooth pattern when compared with that of a neat PS, as illustrated in Figure 9(b–d). This implied that the incorporation of CNs into PS might effectively enhance the wear resistance of PS. The conclusion obtained from the SEM observations is

consistent with the previous studies related to the wear-loss measurement of neat PS and corresponding composites. Introducing CNs may attribute the increase of surface wear resistance of neat PS by the incorporation of CNs to the increase of surface hardness of neat polymer.

CONCLUSIONS

In this article, the series of PCN materials consisting of commercial PS and organoclay platelets were successfully prepared through a melt intercalation approach. The as-prepared PCN materials were subsequently characterized by powder XRD and TEM. Furthermore, the effect of organoclay on three different measurement types of mechanical properties for as-prepared PCN materials such as flexural test, impact test, and micron-nano indenter test were performed and compared. Generally, it exhibited an obvious enhancement of mechanical properties of neat polymer by an incorporated low loading of organophilic clay platelets into a polystyrene matrix base on the evaluation of mechanical properties on as-prepared samples. The wear resistance of PS was found to be effectively enhanced by the incorporation of a low loading of organophilic clay platelets. The surface morphological image for the neat PS and PS-clay after wear resistance test had also been compared and identified by the SEM. We found that

the results showed that while the MMT content is increased, so is all its mechanical properties: flexural modulus, hardness, and wearing. When 5 wt % MMT was added to the PS base materials, we could get the best results increasing 36% in flexural modulus, 32% in hardness, 120% in wear loss, and decreasing 21% in the absorption of impact energy. Moreover, the increase of clay loading up to 5 wt % of as-prepared PCN materials were found to be accompanied with an increase of mechanical strength.

References

1. Tyan, H. L.; Liu, Y. C.; Wei, K. H. *Chem Mater* 1999, 11, 1942.
2. Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Hayyis, R. J.; Manias, E.; Giannelis, E. P.; Hilton, M.; Wuthenow, D.; Phillips, S. H. *Chem Mater* 2000, 12, 1866.
3. Lan, T.; Kaviratna, P. D.; Piannavaia, T. J. *Chem Mater* 1994, 6, 573.
4. Yeh, J. M.; Liou, S. J.; Lai, C. Y.; Wu, P. C.; Tsai, T. Y. *Chem Mater* 2001, 13, 1131.
5. Yeh, J. M.; Liou, S. J.; Lin, C. Y.; Cheng, C. Y.; Chang, Y. W.; Lee, K. R. *Chem Mater* 2002, 14, 154.
6. Yeh, J. M.; Chen, C. L.; Chen, Y. C.; Ma, C. Y.; Lee, K. R.; Wei, Y.; Li, S. *Polymer* 2002, 43, 2729.
7. Yeh, J. M.; Chin, C. P.; Chang, S. J. *Appl Polym Sci* 2003, 88, 3264.
8. Yeh, J. M.; Chin, C. P. *J Appl Polym Sci* 2003, 88, 1072.
9. Yu, Y. H.; Yeh, J. M.; Liou, S. J.; Chang, Y. P. *Acta Mater* 2004, 52, 475.
10. Yu, Y. H.; Yeh, J. M.; Jen, C. C.; Huang, H. Y.; Wu, P. C.; Huang, C. C. *J Appl Polym Sci* 2004, 91, 3438.
11. Yeh, J. M.; Liou, S. J.; Lin, C. G.; Chang, Y. P.; Yu, Y. H. *J Appl Polym Sci* 2004, 92, 1970.
12. Yeh, J. M.; Liou, S. J.; Lu, H. J.; Huang, H. Y. *J Appl Polym Sci* 2004, 92, 2269.
13. Yeh, J. M.; Chen, C. L.; Chen, Y. C.; Ma, C. Y.; Yu, Y. H.; Huang, H. Y. *J Appl Polym Sci* 2004, 92, 631.
14. Yeh, J. M.; Chen, C. L.; Kuo, T. H.; Su, W. F.; Huang, H. Y.; Liaw, D. J.; Lu, H. Y.; Liu, C. F.; Yu, Y. H. *J Appl Polym Sci* 2004, 92, 1072.
15. Yu, Y. H.; Yeh, J. M.; Liou, S. J.; Chen, C. L.; Liaw, D. J.; Lu, H. Y. *J Appl Polym Sci* 2004, 92, 3573.
16. Kim, Y.; White, J. L. *J Appl Polym Sci* 2005, 96, 1888.
17. Kato, C.; Kuroda, K.; Takahara, H. *Clay Clay Miner* 1981, 29, 294.
18. Akelah, A.; Moet, A. *J Mater Sci* 1996, 31, 3189.
19. Akelah, A.; Moet, A. *Mater Lett* 1993, 18, 97.
20. Doh, J. G.; Cho, I. *Polym Bull* 1998, 41, 511.
21. Fu, X.; Qutubuddin, S. *Mater Lett* 2000, 42, 12.
22. Fu, X.; Qutubuddin, S. *Polymer* 2001, 42, 807.
23. Tseng, C. R.; Wu, J. Y.; Lee, H. Y.; Chang, F. C. *J Appl Polym Sci* 2002, 85, 1370.
24. Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Usuki, A. *J Appl Polym Sci* 1999, 74, 3359.
25. Bhimaraj, P.; Burris, D. L.; Action, J.; Sawyer, W. G.; Toney, C. G.; Siegel, R. W.; Schadler, L. S. *Wear* 2005, 258, 1437.
26. Yu, S.; Yu, Z.; Mai, Y. W. *Tribology Int* 2007, 40, 855.
27. Yeh, J. M.; Chen, C. L.; Huang, C. C.; Chang, F. C.; Chen, S. C.; Su, P. L.; Kuo, C. C.; Hsu, J. T.; Chen, B.; Yu, Y. H. *J Appl Polym Sci* 2006, 99, 1576.
28. Kim, T. H.; Jang, L. W.; Lee, D. C.; Choi, H. J.; Jhon, M. S. *Macromol Rapid Commun* 2002, 23, 191.
29. Park, B. J.; Kim, T. H.; Choi, H. J.; Lee, J. H. *J Macromol Sci B Phys* 2007, 46, 341.