

Sound Damping of a Polyurethane Foam Nanocomposite

Chang Hyun Sung and Kyung Sick Lee

Mechanical and Automotive Engineering, University of Ulsan, Ulsan 680-749, Korea

Kyu Se Lee and Seung Min Oh

Ilkwang Industrial Co., Ltd., Ulsan 689-870, Korea

Jae Hoon Kim, Min Seok Kim, and Han Mo Jeong*

Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea

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Abstract: To improve the sound damping effect of flexible polyurethane foam, with an open-cell structure, various plate-like fillers, such as bentonite, organophilic clay and sodium montmorillonite intercalated with poly(ethylene glycol), were incorporated for the creation of nanocomposites. The plate-like fillers effectively improved the sound damping within the high frequency range. The structures of the nanocomposites and foam were examined using X-ray diffraction and scanning electron microscopy. The mechanical properties and flammability of the foams were also examined.

Keywords: foam, polyurethane, nanocomposite, clay, sound damping.

Introduction

Sound damping is a very important component in the design of a comfortable car, because to achieve driving comfort, structural- and air-borne noises should adequately be reduced.¹ The vibrations emanating from the engine or from contact with the road are the primary causes of structural-noise, while the sound of the engine explosion, road noise, or sound of wind generated at high speeds are the causes of air-borne noise.^{1,2} A great portion of the structural-borne noise spans low frequency in the range of 30~500 Hz while air-borne noise is mostly contained in medium and high frequency ranges of 500~8,000 Hz.²

Foams are a very common type of sound damping material, because they can store strain energy caused by sound waves and dissipate a portion of this energy as heat through hysteresis. In addition, sound is also damped by scattering and reflection in the cell of the foam.^{3,4} It is well known that open-cell flexible polyurethane foam is effective in damping air-borne sound.⁵⁻⁸ Consequently, polyurethane (PU) foams are widely used in cars as sound damping materials because they meet a set of conflicting criteria; effective sound damping, low density, inflammability, malleability to form it into various styles and shapes, and the ease of production.^{1,4,5,9} When the density of PU foam was

increased by the incorporation of micro-sized inert fillers, such as barium sulfate, calcium carbonate, silica, or fiberglass, the level of sound damping can be improved even further.^{1,3}

In recent years, polymer/silicate nanocomposites have attracted considerable attention as prospective materials, because of their substantially enhanced physical properties over pristine polymers, even when prepared with a very small amount of layered silicate.^{10,11} These nanocomposites demonstrate improved thermal, mechanical, barrier, and flame-retardant properties. The unique properties of these nanocomposites arise from the maximized interfacial contact between the organic and inorganic phase. Therefore, fillers with a high surface-to-volume ratio are commonly used. Plate-like layered silicate such as montmorillonite, which is composed of stacks of parallel lamellae with a 1 nm thickness and a high aspect ratio, are typically selected.¹²⁻¹⁶ It was reported that the thermal insulation effect of close-cell PU foam can be improved when a layered silicate was integrated into the PU foam, because a plate-like silicate can act as a gas barrier reducing the infusion of air into the foam cells and diffusion of the blowing agent out of the foam cells.^{17,18} However, to the best of our knowledge, there are no reports regarding the effect of layered silicate on sound damping. To this end, we integrated various kinds of montmorillonite into PU foam to examine sound dampening and present the results in this paper.

*Corresponding Author. E-mail: hmjeong@mail.ulsan.ac.kr

Experimental

Materials. Commercial polyol, Nixol SA-120 supplied by Korea Polyol Co., Ltd. was used in the preparation of PU foam. The polyol was synthesized by the stepwise polyaddition of propylene oxide and ethylene oxide onto a starter, glycerol, to yield a triol with a terminal ethylene oxide block. The molecular weight of polyol is 6,000 and the content of ethylene oxide block in polyol is about 15%. The Nixol SA-120 contains 2.4 wt% water which acts as a blowing agent in the foaming process and some amount of catalyst, surfactant, and something else necessary for foaming. Commercial grade methylene diphenyl diisocyanate (MDI, Suprasec 2527) was supplied from Huntsman Co.

The bentonite, Opazil, whose major component is montmorillonite was purchased from Süd-Chemie Korea Co., Ltd. and sodium montmorillonite (Na-MMT) was purchased from Southern Clay Product Inc. Organophilic clay, Cloisite 25A, was also obtained from Southern Clay Product Inc., and it was reported that in this organophilic clay, the cations of natural montmorillonite were replaced by dimethyl, hydrogenated tallow, and 2-ethylhexyl quaternary ammonium ions. The weight loss on ignition of Cloisite 25A is 34%, and the modifier concentration is 95 meq/100 g-clay. The bentonite, Na-MMT, and Cloisite 25A were used after drying at 60°C in a vacuum for 2 days. Another inorganic filler, BaSO₄, whose average particle size is 325 mesh was purchased from Lakavisuth Co. Poly(ethylene glycol) (PEG), whose molecular weight was 200, was purchased from Wako Pure Chemical Industries Ltd. Acetonitrile (Aldrich) and methanol (Aldrich) were used as received.

Na-MMT intercalated with PEG (Na-MMT/PEG) was prepared using a 1 : 1 (by volume) acetonitrile/methanol solvent system.^{19,20} Briefly, 3 g of PEG was dissolved in 100 mL of the solvent mixture, which was stirred with 7 g of Na-MMT for 1 day at room temperature. The intercalated compound was separated with a centrifuge, and repeatedly washed with acetonitrile and methanol to remove any non-intercalated physisorbed PEG.¹⁹ The newly prepared compound was dried at 60°C for 2 days in a vacuum prior to use. The weight loss by pyrolysis in a furnace at 600°C showed that the amount of PEG in the gallery of Na-MMT was 0.16 g/g -Na-MMT. The Na-MMT/PEG was reported to have a high stability, and thus the intercalated PEG cannot be replaced by organic compounds with a high affinity for Na-MMT, such as dimethyl sulfoxide.^{19,20} The hydroxyl group of PEG intercalated in Na-MMT can participate in the chain extension by the reaction with MDI in the foaming process.

Preparation of PU Foam. Slab foam was prepared by the one-shot, free-rise method, according to the recipe shown in Table I. The reference sample B-0 was prepared as follows: a mixture consisting of polyol and inorganic filler, BaSO₄, was mixed thoroughly with MDI using a high speed mixer. The mixture was poured into a mold and allowed to rise freely. The inner size of mold was 10 mm in height, 200 mm wide, 200 mm in length, and the temperature of the mold was controlled at 60°C.⁴ Other samples were prepared in a similar manner except that, as noted in Table I, the amounts of BaSO₄, bentonite, organophilic clay, and Na-MMT/PEG were adjusted as main variables in B series, S series, R series, and P series, respectively. The density of all the sam-

Table I. Recipe for the Preparation of PU Slab Foam

Designation Code	Feed (Weight Ratio)					
	MDI (Suprasec 2527)	Polyol (Nixol SA-120)	BaSO ₄	Bentonite	Organophilic Clay (25A)	Na-MMT/PEG
B series						
B-0	32.0	88.9	11.1	-	-	-
B-22	32.0	87.0	13.0	-	-	-
B-43	32.0	85.1	14.9	-	-	-
B-63	32.0	83.3	16.7	-	-	-
S series						
S-22	32.0	87.0	10.9	2.2	-	-
S-43	32.0	85.1	10.6	4.3	-	-
S-63	32.0	83.3	10.4	6.3	-	-
R series						
R-22	32.0	87.0	10.9	-	2.2	-
R-43	32.0	85.1	10.6	-	4.3	-
R-63	32.0	83.3	10.4	-	6.3	-
P series						
P-22	32.0	87.0	10.9	-	-	2.2
P-43	32.0	85.1	10.6	-	-	4.3

ples was controlled to be 85 kg/m^3 by adjusting the amount of feed poured into the mold.

Measurements. The sound absorption ratio was measured over the frequency range of 500–6,300 Hz by a standing wave ratio method in a duct (Acoustic Duct of the Scien Co.) with two microphones. The slab foam, of 30 mm diameter and 10 mm thickness, was set on the rigid termination at the opposite side of speaker for the measurement of the absorption ratio, α defined by the following eq. (1).^{1,21}

$$\alpha = 1 - \frac{V}{I} \quad (1)$$

where

V = reflected sound energy

I = initial sound energy

The slab foam was cut with a knife and the cross-section was observed with a scanning electron microscope (SEM, JSM 820) to examine the cell structure. The cross-section was sputtered with gold before observation.

X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Rigaku, RAD-3C) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) as the X-ray source. The diffraction angle was scanned from 1° at a rate of $1.2^\circ/\text{min}$.

Tear strength and tensile strength of the slab foam were measured according to KS M 6518 with a tensile tester (Instron 3365) at an elongation speed of 200 mm/min. The specimens for tear and tensile strength measurements were Type B and No. 1 of KS M 6518, respectively.

Flammability was determined according to KS B 9252-1978; a specimen was exposed to a burner flame for 15 sec, and the burn rate was calculated by dividing the length from line A to line B over which the flame travels by the time necessary for the flame to travel that distance. The distances from the end of the specimen, where the flame burner touches, to line A and line B are 38 mm and 254 mm, respectively. When the specimen does not burn, even though it was touched with the flame burner for 15 sec, the specimen is classified as nonflammable. When the flame does not propagate more than 50 mm from line A and is extinguished within 60 sec, the specimen is classified as self-extinguishing.

Results and Discussion

XRD. The XRD pattern of Figure 1(a) shows that Na-MMT has a peak around $2\theta = 7.0^\circ$, however, Figure 1(b) shows that this peak moves to a lower angle, $2\theta = 6.5^\circ$, when PEG is intercalated in the gallery of Na-MMT. These results indicated that the basal plane spacing d_{001} , which was calculated by Bragg's law, where $d_{001} = \lambda/2 \sin \theta$, was increased from 12.8 to 13.6 \AA by the intercalation of PEG.^{19,20,22,23} The PU foam modified with Na-MMT/PEG, P-43 has a shoulder around $2\theta = 5^\circ$ (Figure 1(d)). This shows

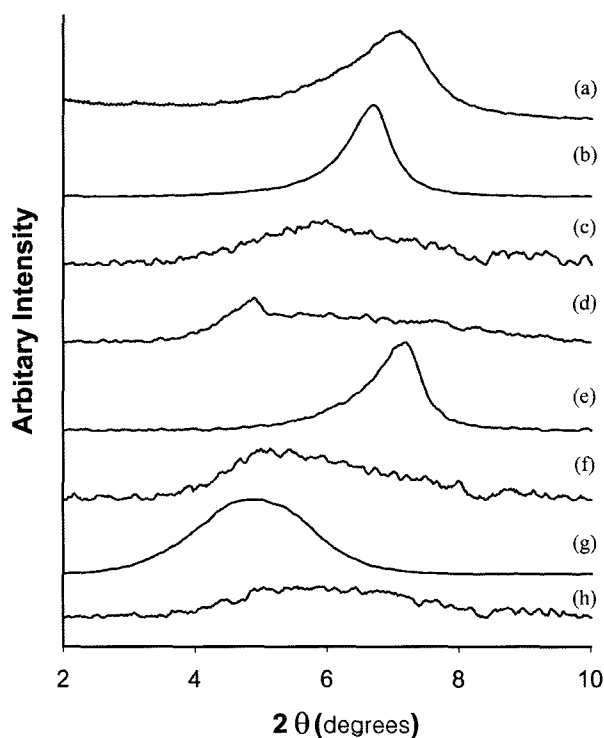


Figure 1. XRD patterns of (a) Na-MMT, (b) Na-MMT/PEG, (c) B-0, (d) P-43, (e) bentonite, (f) S-43, (g) organophilic clay, and (h) R-43.

that the gallery height had swelled further to around 17.7 \AA after the foaming process. The bentonite has a peak at $2\theta = 7.1^\circ$ (Figure 1(e)), and this peak position is similar to that of Na-MMT, because the major component of bentonite is montmorillonite. The PU foam modified by bentonite, S-43, also shows a broad shoulder around $2\theta = 5^\circ$ (Figure 1(f)) similar to that of P-43. These results show that both bentonite and Na-MMT have similar structures in the PU foam which had a gallery height of about 17.7 \AA by the intercalation of PEG or the PU chain.

In general, two idealized polymer-layered silicate nanocomposites structures are possible: intercalated and exfoliated. Intercalated structures are self-assembled, well-ordered, and multilayered structures in which the extended polymer chains are inserted into the gallery space between parallel individual silicate layers. Because these structures usually retain multilayered features with alternating polymer-silicate layers, an increased d-spacing between the silicate layers can be detected by X-ray diffraction (XRD). In the exfoliated structure, the individual silicate layers are delaminated and randomly dispersed in the polymer matrix separately. The exfoliated structures no longer give a coherent wide-angle ($2\theta > 1^\circ$) XRD signal, because the distances between the silicate layers are expanded far apart and the layers are sufficiently disordered.²³⁻²⁵ So, the results of XRD explained before support that the PU foams are PU/mont-

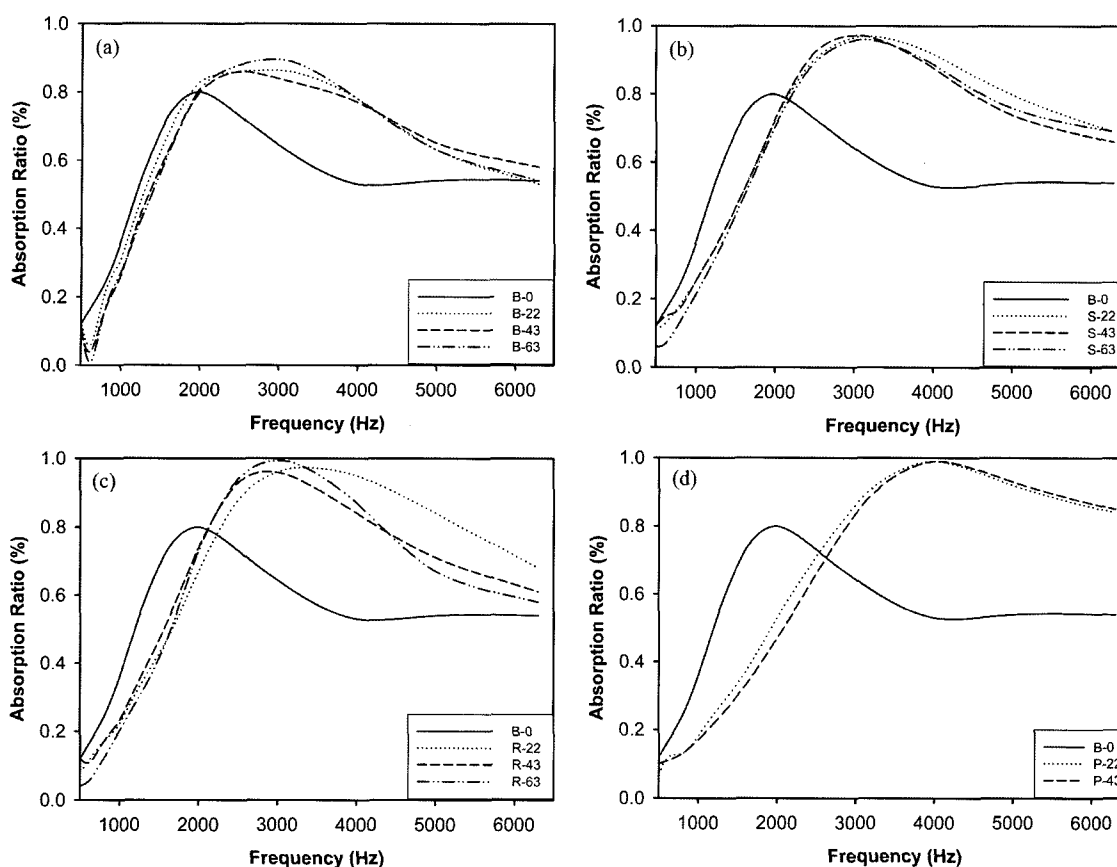


Figure 2. Sound absorption ratios of PU foams: (a) B series, (b) S series, (c) R series, and (d) P series.

morillonite nanocomposites with intercalated structure.

The organophilic clay has a peak around $2\theta = 5^\circ$ (Figure 1(g)). When the PU foam was modified with organophilic clay (R-43), the peak intensity around $2\theta = 5^\circ$ in Figure 1(h) was increased compared with that of the reference sample, B-0. This result shows that gallery height increase of the organophilic clay by the intercalation of the PU segment was not obviously evident in this PU foam.

Sound Damping. Figure 2 shows the variation of sound damping when the PU foam was modified by various kinds fillers. As the content of BaSO₄ was increased, we can see that the maximum value of the sound absorption ratio increased (Figure 2(a)). Figures 2(b)–2(d) show that this variation was more evident when the inorganic fillers, which have plate-like structures, such as bentonite, organophilic clay, or Na-MMT/PEG, were used.

It was reported that, when aluminum foil or a flexible plastic layer is inserted in the PU foam, the sound damping effect of the PU foam can be enhanced.^{5,6} When the fillers are dispersed in the wall of the foam, we can anticipate that the energy dissipation as heat through hysteresis can be increased, because the wall of the PU foam should move together with the massive inorganics when it recovers its deformation caused by sound waves. We can also anticipate

that the sound damping by scattering or reflection would be increased when the stiffness of the wall is increased²⁶ or when the inorganics or plastic films act as another wall for sound blocking. So, the results of Figure 2 support the notion that sound damping can be increased by a fine dispersion of inorganics in the cell wall of the PU foam, and this effect is more evident when the inorganics have a plate-like structure and high aspect ratio such as that in montmorillonite. Our results in Figure 2 are similar to those of a previous report in that this sound damping, due to massive plate-like additive, was advantageously observed at higher frequencies, but exhibited the disadvantages of resonance at a lower frequency.⁶ So, we feel that further study is necessary for a detailed explanation of this reduced sound damping behavior at low frequency.

SEM. The morphology observed by SEM in Figure 3, shows that all the foams have an open-cell structure. The cell size of S-43 is evidently reduced compared to a reference sample B-0, probably due to the nucleating effect of bentonite,¹⁷ however, the cell size of other foams is similar with that of B-0. The cell size can influence the sound damping of the PU foam,^{2,5} but our results show that the reduction of cell size is not the major cause of enhanced sound damping when modified with fillers.

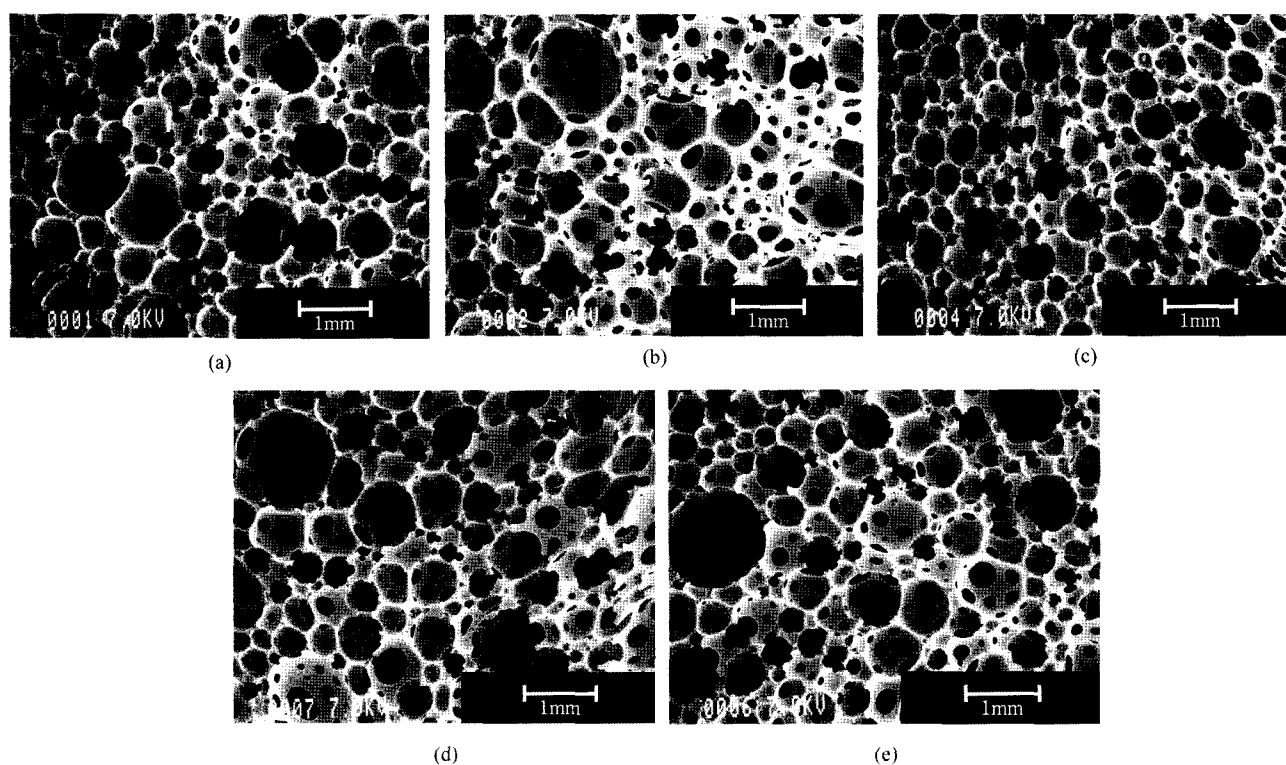


Figure 3. SEM micrographs of the cross-section of PU foams: (a) B-0, (b) B-43, (c) S-43, (d) R-43, and (e) P-43.

Mechanical Properties and Flammability. Table II shows that tear strength and tensile strength generally increase as the content of fillers, BaSO₄, bentonite, or organophilic clay increase, with some exceptions, and that elongation at break is concomitantly decreased. This shows the reinforcing

effect of the fillers. However, tear strength and tensile strength are reduced and elongation at break is increased when Na-MMT/PEG is used as a modifier. This shows that PEG intercalated in the gallery of Na-MMT softens the foam.

Table II. Mechanical Properties and Flammability of the PU Foam

Sample	Tear Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Flammability (mm/min)
B series				
B-0	2.74 ± 0.07	0.141 ± 0.004	161 ± 5	self-extinguishing
B-22	2.82 ± 0.13	0.142 ± 0.007	148 ± 16	self-extinguishing
B-43	2.93 ± 0.09	0.150 ± 0.002	146 ± 7	self-extinguishing
B-63	2.94 ± 0.20	0.157 ± 0.016	137 ± 12	self-extinguishing
S series				
S-22	2.73 ± 0.30	0.139 ± 0.017	149 ± 8	self-extinguishing
S-43	3.15 ± 0.38	0.141 ± 0.007	147 ± 6	self-extinguishing
S-63	3.56 ± 0.34	0.168 ± 0.005	141 ± 9	self-extinguishing
R series				
R-22	2.83 ± 0.22	0.140 ± 0.005	157 ± 10	55
R-43	3.10 ± 0.37	0.154 ± 0.004	149 ± 1	62
R-63	3.45 ± 0.51	0.161 ± 0.019	145 ± 5	78
P series				
P-22	2.56 ± 0.43	0.125 ± 0.004	167 ± 11	self-extinguishing
P-43	2.63 ± 0.26	0.127 ± 0.009	164 ± 12	self-extinguishing

The flammability of layered silicate/polymer nanocomposites is generally reduced compared to pure polymer, because layered silicate-reinforced carbonaceous char is formed during the combustion of nanocomposites, and this multilayered carbonaceous-silicate structure can act as an excellent insulator and mass transport barrier, slowing the escape of the volatile products generated during decomposition.^{25,27-29} However, Table II shows that the flammability of the PU foam increased, compared to reference sample B-0, in R-series where an organophilic clay was added as a modifier. When we consider that organophilic clay contains about 34% organic ammonium ions, this ion seems to be the cause of increased flammability. That is, it was reported that organic ammonium ions can be easily degraded into α -olefin and amine via Hofmann elimination, and the α -olefin can easily combine with oxygen to give peroxoradicals.^{30,31} These degradation and accompanied reactions seem to be the causes of enhanced flammability.

Conclusions

Our experimental results showed that the sound damping of PU foam can be enhanced by modifying it with plate-like fillers, such as montmorillonite, to obtain a nanocomposite with an intercalated structure. The finely dispersed massive plate-like filler can increase energy dissipation as heat through hysteresis and the scattering or reflection of sound in the cell. These features may be the causes of the improved sound damping observed in the nanocomposites.

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References

- (1) J. J. Zwinselman and J. J. Laux, *Polym. Mater. Sci. Eng.*, **60**, 827 (1989).
- (2) N. Park, Y. Kim, and C. Park, *J. Kor. Ind. Eng. Chem.*, **8**, 197 (1997).
- (3) D. Klemmner, D. Sophiea, B. Suthar, K. C. Frisch, and V. Sendjarevic, *Polym. Mater. Sci. Eng.*, **65**, 82 (1991).
- (4) D. K. Lee, L. Chen, A. Sendjarevic, V. Sendjarevic, K. C. Frisch, and D. Klemmner, *J. Cellular Plastics*, **27**, 135 (1991).
- (5) Y. Imai and T. Asano, *J. Appl. Polym. Sci.*, **27**, 183 (1982).
- (6) R. Bohm and R. Josel, UK Patent GB 2138012A (1984).
- (7) P. Falke, I. Rotermund, K. Schmutzer, and K. Schmalzer, US Patent 6316514B1 (2001).
- (8) P. Scudieri, US Patent 0025487A1 (2006).
- (9) D. J. Lovell, C. Y. Chan, and S. E. Diaczun, US Patent 00297788A1 (2006).
- (10) T. J. Pinnavaia and G. W. Beall (Editors), *Polymer-Clay Nanocomposites*, John Wiley & Sons, New York, 2000.
- (11) L. A. Utracki, *Clay-Containing Polymeric Nanocomposites*, Rapra Technology Limited, Shawbury, 2004.
- (12) E. P. Giannelis, *Appl. Organometal. Chem.*, **12**, 675 (1998).
- (13) S. Subramani, J. M. Lee, J. H. Kim, and I. W. Cheong, *Macromol. Res.*, **13**, 418 (2005).
- (14) Y. S. Choi, Y. K. Kim, and I. J. Chung, *Macromol. Res.*, **11**, 418 (2003).
- (15) S. Y. Park and Y. H. Cho, *Macromol. Res.*, **13**, 156 (2006).
- (16) J. H. Park, W. N. Kim, H. S. Kye, S. S. Lee, M. Park, J. Kim, and S. Lim, *Macromol. Res.*, **13**, 367 (2006).
- (17) T. Widya and C. Macosko, *J. Macromol. Sci.-Phys.*, **44**, 897 (2005).
- (18) J. E. Kresta, J. H. Wu, and R. M. Crooker, US Patent 6518324B1 (2003).
- (19) P. Aranda and E. Ruiz-Hitzky, *Chem. Mater.*, **4**, 1395 (1992).
- (20) J. Wu and M. M. Lerner, *Chem. Mater.*, **5**, 835 (1993).
- (21) C.-M. Lee and Y. S. Wang, *J. Sound Vibration*, **298**, 350 (2006).
- (22) E. Ruiz-Hitzky and P. Aranda, *Adv. Mater.*, **2**, 545 (1990).
- (23) H. M. Jeong, M. Y. Choi, and Y. T. Ahn, *Macromol. Res.*, **14**, 312 (2006).
- (24) C. Zeng and L. J. Lee, *Macromolecules*, **34**, 4098 (2001).
- (25) J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris Jr., E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. H. Phillips, *Chem. Mater.*, **12**, 1866 (2000).
- (26) H. Park, A. K. Mohanty, L. T. Drzal, E. Lee, D. F. Mielewski, and M. Misra, *J. Polym. Environ.*, **14**, 27 (2006).
- (27) A. B. Morgan, R. H. Harris Jr., T. Kashiwagi, L. J. Chyall, and J. W. Gilman, *Fire Mater.*, **26**, 247 (2002).
- (28) G. Beyer, *Polym. Polym. Compos.*, **13**, 529 (2005).
- (29) T. Kashiwagi, F. Du, J. F. Douglas, K. I. Winey, R. H. Harris Jr., and J. R. Shields, *Nature Mater.*, **4**, 928 (2005).
- (30) D. L. VanderHart, A. Asano, and J. W. Gilman, *Chem. Mater.*, **13**, 3796 (2001).
- (31) W. Xie, Z. Gao, W. Pan, D. Hunter, A. Singh, and R. Vaia, *Chem. Mater.*, **13**, 2979 (2001).