Nanoclay Reinforced Rigid Polyurethane Foams

S. H. Kim,[1] M. C. Lee,[2] H. D. Kim,[2] H. C. Park,[3] H. M. Jeong,[4] K. S. Yoon,[4] B. K. Kim[1]

[1]*Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea*
[2]*Department of Organic Materials System Engineering, Pusan National University, Busan 609-735, Korea*
[3]*School of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea*
[4]*Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea*

Received 29 June 2009; accepted 16 January 2010
DOI 10.1002/app.32116

ABSTRACT: Clay was intercalated and exfoliated by neutralized dimethylol butanoic acid (DMBA) and used to fabricate rigid polyurethane foam (RPUF)/clay nanocomposites. Cream time, gel time, and tack-free time increased with the addition and increasing amount of clay whereas foam density and compression strength decreased. Cell size, closed cell content, volume change upon heating and cooling, and thermal conductivity of the foam decreased with the addition and increasing amount of clay with a minimum at 2 pphp (parts per 100 polyol by weight). The glass transition and decomposition temperatures increased with increasing clay content due to the restricted motion of chains and barrier property of the clay platelets. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1992–1997, 2010

Key words: polyurethane foam; nanocomposite; morphology; thermal stability; density

INTRODUCTION

Polyurethanes (PUs) are a unique class of polymers, which have a wide range of applications because their properties can be readily tailored by the variations of their components.[1–3] PUs are used as foams, coatings, adhesive, elastomers, and fibers. Among them rigid polyurethane foams (RPUFs) find numerous applications as insulations of refrigerators, freezers, piping, tanks, and ship building, and LNG cargos.[4] In such application, high compression strength especially at low temperature and thermal insulation are properties of prime importance.[5]

Conventional blowing agents such as monofluorotrichloromethane (R11) and difluorodichloromethane (R12) have recently been regulated in many countries from the environmental considerations.[6–8] Consequently, the use of environmentally friendly blowing agents has become an important and urgent issue in the synthesis of PU foam[9,5] Water can in part replace such environmentally hazardous blowing agents. However, the excessive use of water causes a negative pressure gradient due to the rapid diffusion of CO_2 through the cell wall causing cell deformation.

We have earlier reported the effects of hydroxyl value and functionality of polyol,[10,11] isocyanate index,[12] surfactant,[13] and type of blowing agent[14] in the preparation of RPUF using environmentally friendly blowing agents. As most RPUF are designed for thermal insulation, further efforts are desired to enhance the insulation property of the foam.

PUFs/caly nanocomposites are comparatively new class of composite materials where at least one phase has dimension in the nanosize range.[15,16] In these composites, clay is reported to act as cell opener[17,18] where ultrasonic treatment often gave homogeneous cell size and improved dimensional stability.[19,20] High mechanical and thermal properties compared with conventional composites are also expected by the filler effect of clay.[16] However, it is difficult to achieve complete exfoliation of the silica layers due to the strong electrostatic interactions between silicate layers and intragallery cations.[21]

In this study, we synthesized PUF/clay nanocomposites using an environmentally friendly physical blowing agent. The intercalated and exfoliated layers of clay were prepared by using neutralized dimethylol butanoic acid (DMBA). The foaming process was followed, and the foams were analyzed in terms of cell structure, density, thermal conductivity, mechanical, and thermal properties.

EXPERIMENTAL

Raw materials

Two types of propylene oxide based polyols, viz. HR-450P (hydroxyl value = 450, equivalent weight = 124.7) and KR-403 (hydroxyl value = 400, equivalent weight = 140) were supplied by KPX, formerly

---

Correspondence to: B. K. Kim (bkkim@pnu.edu).

Journal of Applied Polymer Science, Vol. 117, 1992–1997 (2010)

TABLE I
Formulations to Prepare RPUFs

Samples	Clay (pphp)	DMBA (g)	TEA (g)	HR-450P (pphp)	KR-403 (pphp)	HFC 365mfc (pphp)	B 8409 (pphp)	33LV (pphp)	PMDI (pphp)
N00	0	0	0	60	40	12	2	0.6	114.3
N05	0.5	0.2	0.169						
N10	1	0.4	0.338						
N20	2	0.8	0.676						
N40	4	1.6	1.353						

The formulation is based on 100 parts of the polyol by weight (pphp).

Korea Polyol (Korea). HR-450P was synthesized using sucrose and glycerin as coinitiators, whereas KR-403 used toluenediamine as initiator. High functional polymeric 4,4′-diphenylmethane diisocyanate (PMDI) was provided by Kumho Mitsui Chemicals (Korea). HFC 365mfc as physical blowing agent was provided by Solvay Chemicals (Belgium). 33LV (Air Products) was used as gelling catalyst. Silicon surfactant (B 8409) was provided by Goldschmidt. Polyols were dehydrated at 90°C for 24 h in a vacuum oven before use. Dimethylol butanoic acid (DMBA, Aldrich) was dried at 50°C for 48 h in vacuo. Triethylamine (TEA, Aldrich) was dried over 4-Å molecular sieves before use. Cloisite 30B was purchased from Southern Clay Products. The cation exchange capacity of the Cloisite 30B is 90 meq/100 g of the clay.[22] Cloisite 30B was dehydrated at 90°C for 48 h in a vacuum oven before use. Other chemicals were used as received.

Preparation of samples

Polyol and DMBA were first mixed using a four-necked separable flask equipped with a mechanical stirrer, thermometer, condenser, and nitrogen injection tube. Then the premixed polyol was cooled to 60°C, and a neutralizing agent, i.e. TEA was added and stirred for 2 h while maintaining the temperature at 30°C. Polyol containing DMBA and Cloisite 30B was mixed at 60°C for 5 h. The basic formulations to prepare the foams are given in Table I. The foams were synthesized by one shot method.[23] That is, all materials shown in the Table I were put into a mixing cup and mixed thoroughly at 3000 rpm and at room temperature until they become homogeneous. The NCO index (isocyanate equivalents/polyol equivalents) was fixed at 1.10 based on our earlier work.[12] Then the mixtures were poured into an open mold (200 mm × 200 mm × 100 mm) and cured for 1 week at room temperature. The reaction time was measured by a digital stop watch. The closed celled content was determined by an air pycnometer following ASTM D 3574 with specimen dimension, 50 mm × 50 mm × 25 mm. Density of the foam was measured according to the ASTM D 1622 with sample size of 30 mm × 30 mm × 30 mm (Width × Length × Thickness), and average of at least five measurements was taken to report. Thermal conductivity was measured using HC-074 (Laser Comp) according to the ASTM C 518. The cell morphology was observed under a scanning electron microscopy (SEM, HITACHI S3500N). Samples were cryogenically fractured in liquid nitrogen and gold sputtered before they were scanned in the free rising direction. Thermogravimetric analysis (TGA, TA instruments, TGA Q50) was done using 8–10 mg of sample, which was put in an alumina crucible and heated at 10°C/min[24] under N_2 atmosphere, where the flow rate of N_2 was 60–40 L/min. Thermal properties were measured using a differential scanning calorimeter (DSC, Du Pont 9900). Samples were sealed in DSC pan using a crimping and welding press (Du Pont). The DSC thermograms were taken from 20 to 250°C at heating rate of 20°C/min. The distribution of clay layer in the polyol/clay nanocomposites was measured by X-ray diffractometer (X′pert Pro). A Cu$K\alpha$ (wavelength of 1.54 Å) was used and the samples were scanned in the range of 0.5–10°. Mechanical properties were measured using a Universal Testing Machine (Ametek, Lloyd) at room temperature. Compression strength was determined by ASTM D 1621 at a crosshead speed of 3.00 mm/min with the sample dimension of 30 mm × 30 mm × 30 mm ($W \times L \times T$). Dimensional stability was measured at 70 and −30°C for the duration of 24 h following ASTM D 2126.

RESULTS AND DISCUSSION

XRD pattern

The Cloisite 30B is a natural montmorillonite modified with a quaternary ammonium salt. So, ionic interactions are expected between the ammonium ions and carboxylic anions (COO—) of DMBA, which was used to synthesize PU foams. The neutralized DMBA is expected to effectively breakup the clay agglomerates and exfoliate the clay layers. Figure 1 shows the wide angle X-ray diffraction patterns of the polyol/clay composites. It is seen that the intensity and diffraction angle (2θ) of the characteristic clay peak decreases according to

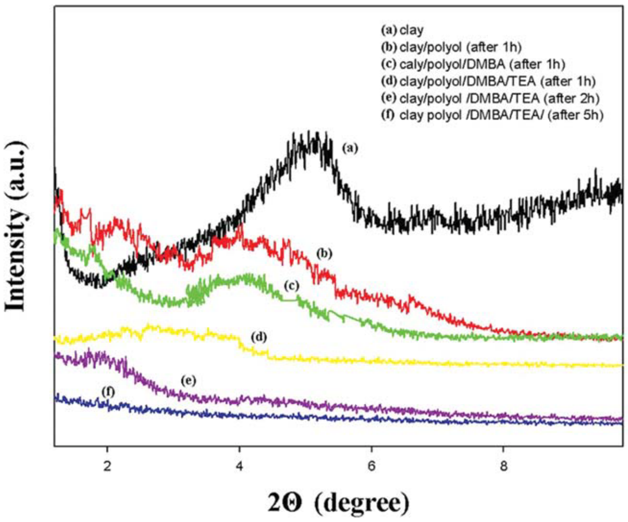

Figure 1 XRD patterns of clay and PUF/Clay Nanocomposites: (a) Clay; (b) Clay/Polyol (after 1 h); (c) Clay/Polyol/DMBA (after 1 h); (d) Clay/Polyol/DMBA/TEA (after 1 h); (e) Clay/Polyol /DMBA/TEA (after 2 h); (f) Clay Polyol/DMBA/TEA (after 5 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Clay > Clay/Polyol > Caly/Polyol/DMBA > Clay/Polyol/DMBA/TEA

The order indicates that the *d*-spacing progressively increases with the addition of polyol, carboxylic acid, and neutralized acid. In 5 h of mixing, characteristic peak of clay disappears for the neutralized sample and the layers are presumably exfoliated completely (Fig. 1).

Kinetics of foam formation

Kinetics of the foam formation are followed by the change of the physical properties, such as cream time, gel time, and tack-free time.[23,25] The cream time corresponds to the start of bubble rise and hence color of the mixture becomes cream-like from dark brown due to the formation of bubbles. Gel time is the starting point of stable network formation by intensive allophanate cross-links as well as urethane and urea linkages. At the tack-free time, the outer surface of the foam loses its stickiness and the foam can be removed from the mold. Table II shows that cream time, gel time, and tack-free time is increased with increasing nanoclay content. The decreased reaction rate indicates that the clay layers provide hindrance for reactions.

Density

All of the properties of the composites are tabulated in Table II. Density is a most important parameter to control the mechanical and thermal properties of closed celled foams.[26,27] Table II shows that the foam density slightly decreases with clay at low and rapidly at high content. It implies that clay acts as a blowing agent for the PU attributed to the interlayer bound waters.[24] And the gases formed between the layers are hard to come out as their movement is interrupted by the clay layers, which give barrier effect.

Cell morphology and foam diameter

Figure 2 shows the SEM morphology of the cell as a function of clay content with their average size and closed cell content in Table II. It is seen that the foams consist of spherical and polyhedral shape, and the average cell size decreases as the clay content increases showing a minimum at 2 pphp. It means that clay acts as nucleating agent. The increase of cell size and closed cell content at 4 pphp reflects poor dispersion of the clay at high clay content.

Compression strength

The compression strength is closely related to the dimensional stability of closed celled foams. As the temperature goes up, gas pressure inside the cell increases and the pressure difference relative to the

TABLE II
Reactivity and Foam Properties

	N00	N05	N10	N20	N40
Cream time (s)	40	49	55	70	100
Gel time (s)	89	100	110	122	168
Tack-free time (s)	204	214	225	255	280
Density (kg/m^3)	112.5	111.5	111.5	108.8	97.4
Cell sizes (μm)	135	123.6	117.5	111.4	114.6
Closed cell content (%)	95.5	94.46	93.92	93.78	94.3
Compression strength (kg/m^2)	12.98	12.68	11.62	11.25	10.07
Volume change (%) 70°C	0.88	0.64	0.62	0.61	0.65
−30°C	−0.4	−0.32	−0.29	−0.25	−0.3

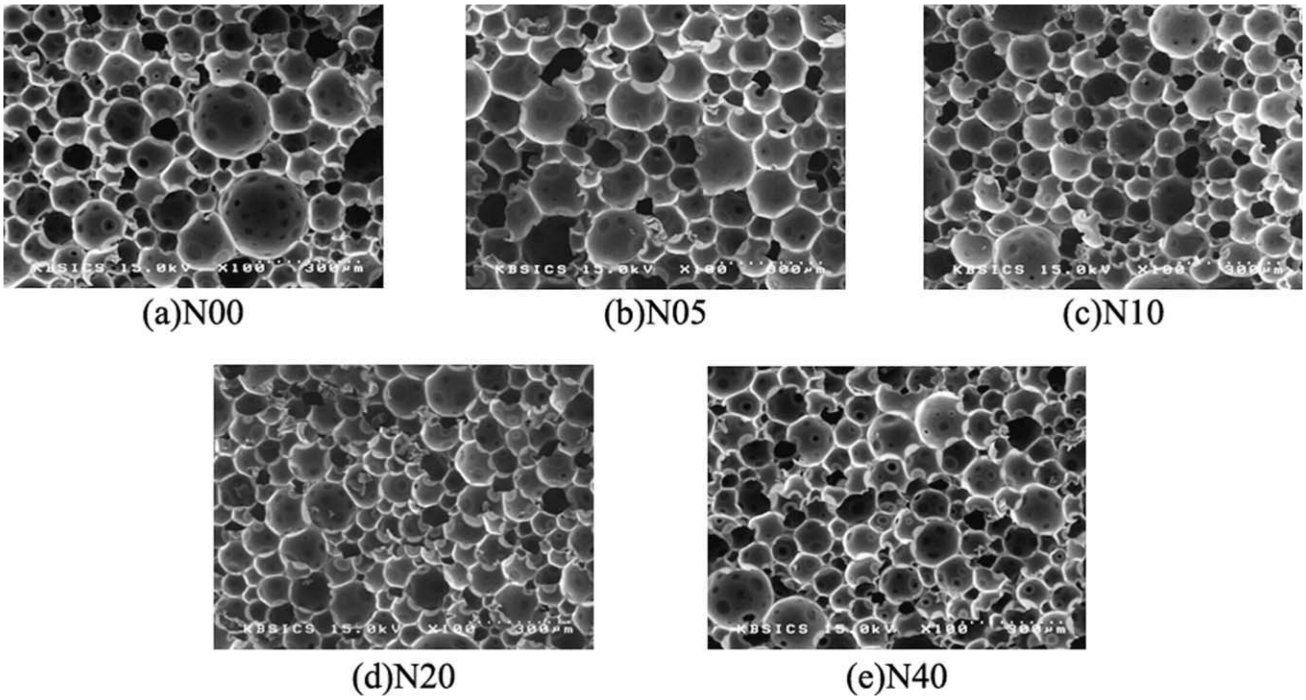
(a)N00 (b)N05 (c)N10 (d)N20 (e)N40

Figure 2 SEM morphology of PUF/clay nanocomposites vs clay content.

atmospheric pressure becomes great. If the foam is to be dimensionally stable under these conditions, the compression strength must be greater than the pressure rise.[26] Minimum compression strength of 0.1 MPa is generally recommended for closed cell foam.[23] Table II shows that the compression strength of the composite generally decreases with increasing clay content owing mainly to the decreased density of the foam.

Dimensional stability

Closed cell foams shrink at low temperature and expand at high temperature. Typically, less than 1% of volume change is desired for sufficient strength. It is seen that the volume changes generally decrease with increasing clay content and even the largest change is less than 1%. The decrease is closely related to the increased glass transition temperature (T_g) of the foam that follow as clay would interrupt chain mobility of the foam. The shrinkage at -30°C is smaller than the expansion at 70°C due probably to the great elasticity of crosslinked cell wall at low temperature. The slight increase at 4 pphp clay is perhaps due to the poor dispersion of the clay at high content.

Thermal conductivity

Heat conduction through the closed cell foams can be approximated by a series model, which is composed of polymer walls and gas cells in series.[28] Conductive heat flux (q) through the composite wall is given by

$$q = \frac{\Delta T}{R} \tag{1}$$

where ΔT is the temperature drop across the foam and R is the conduction resistance given by the following equation.

$$R = \sum_{i=1}^{n} \left(\frac{X_{W,i}}{k_W} + \frac{X_{G,i}}{k_G} \right) \tag{2}$$

Here $X_{W,i}$ and $X_{G,i}$ are the cell wall thickness and cell dimension, and n is the number of polymer walls, respectively. For uniform cells, wall thickness ($X_{W,i}$) and cell dimension ($X_{G,i}$) are constant to give

$$R = n \left(\frac{X_W}{k_W} + \frac{X_G}{k_G} \right) \tag{3}$$

In typical closed cell foam, the polymer walls occupy 3–6 vol % of the foam. In addition, the conductivity of the polymer is much greater than that of the blowing gas. So, the first term, viz. polymer wall resistance can be neglected to give

$$R = n \left(\frac{X_G}{k_G} \right) \tag{4}$$

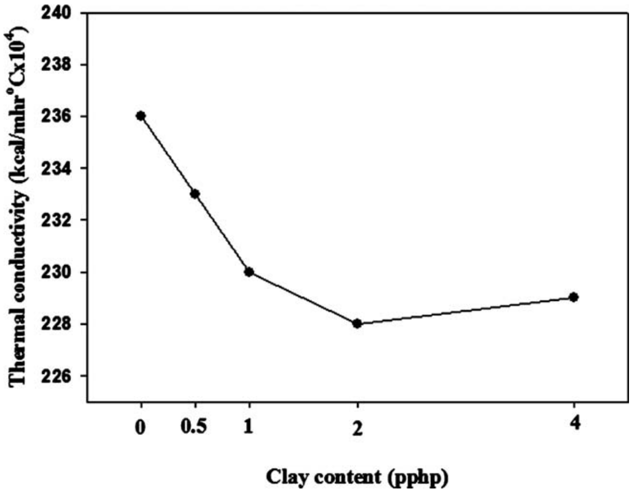

Figure 3 Thermal conductivities of PUF/clay nanocomposites vs clay content.

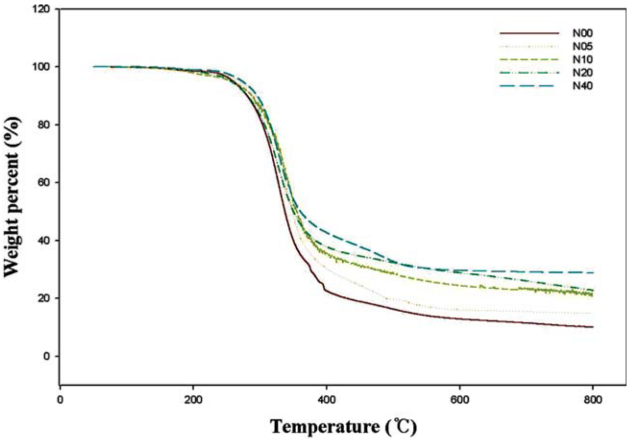

Figure 5 TGA thermograms of PUF/clay nanocomposites vs clay content. (Captions are given in Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The above simple analysis shows that the thermal insulation of closed cell foams increase linearly with the number of closed cells, i.e., effect of insulation increases as the cell size decreases.

Thermal conductivity (*k*) which is commonly called as *k*-factor is a most important property of foam for insulation application. The thermal conductivity of our foam decreases linearly with increasing clay content up to 1% clay (Fig. 3). The decrease is mainly due to the decreased cell size giving a large number of cell (*n*) as analyzed above. However, the conductivity shows an increase at high clay content. This may imply that the wall resistance should be considered along with the increased vol % of the foam. Overall, the effect of clay on thermal conductivity is based on the effect of clay on cell size. That is, conductivity decreased as the cell size decreased up to 2 pphp clay, beyond which cell size increased and conductivity also increased. This implies that the cell size governs the thermal conductivity of the present rigid PU foam. The reason for this would be the small amount of clay incorporated and small volume fraction of cell wall compared with void fraction. As usual for insulation foam, reduction of cell size is a traditional approach to obtain high insulation.

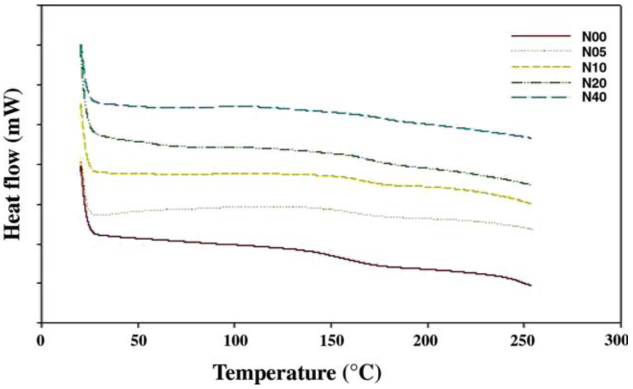

Figure 4 DSC thermograms of PUF/clay nanocomposites vs clay content. (Captions are given in Table I). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal properties

Figure 4 shows the DSC thermograms of the composites. The glass transition temperature of the foam increases with increasing the clay content caused by the restricted mobility of the chain. Notably, at 4 pphp, the glass–rubber transition becomes broad.

Figure 5 shows TGA curves of the nanocomposite where the 10% weight loss temperature is increased by about 10°C in composites due to the barrier effect of clay platelets. It can also be noticed that the final weight loss of the nanocomposite foams becomes smaller with clay. This beneficial effect can be explained by a decrease in the diffusion of oxygen and volatile products throughout the nanocomposite material. In the presence of the clay layers, the pathway of the diffusing gas is remarkably extended.

CONCLUSIONS

It was found that clay was effectively intercalated and exfoliated by carboxylic anions to give rigid polyurethane foam (RPUF)/clay nanocomposite.

Cream time, gel time, and tack-free time increased with the addition and increasing amount of clay indicating that clay interrupts forming and gelling reactions. Foam density monotonically decreased as the clay content increasd due to the additional blowing by the bound water, where the gas formed are entrapped between the layers to result in decrease of foam density, compression strength, and thermal conductivity.

Cell size, closed cell content, volume changes upon cooling and heating decreased with clay showing a minimum at 2 pphp caly. Decrease of cell size is caused by the nucleating effect of clay, where smaller volume change with temperature is due to the increased chain rigidity as noted from the increased T_g from DSC measurements. The unusual results shown at 4 pphp clay are perhaps due to the poor dispersion of the clay at high content.

The thermal conductivity of the composite foam decreased linearly with increasing clay content up to 1% clay due mainly due to the decreased cell size and increased number of cell (n). On the other hand, the conductivity upturn at high clay content is interpreted in terms of wall resistance, which becomes significant at high clay content.

References

1. Hapburn, C. Polyurethane Elastomers; Elsevier: Oxford, 1991.
2. Kim, B. K.; Baek, S. H. J Polym Sci Part A: Polym Chem 1999, 37, 2703.
3. Goods, S. H.; Neuschwanger, C. L.; Whinnery, L. L.; Nix, W. D. J Appl Polym Sci 1999, 74, 2724.
4. Cao, X.; Lee, L. J.; Widya, T. C. Polymer 2005, 46, 775.
5. Mondal, P.; Khakhar, D. V. Macromol Symp 2004, 216, 241.
6. Li, X. B.; Cao, H. B.; Zhang, Y.; Guan, T. J Appl Polym Sci 2006, 102, 4149.
7. Antolini, B.; Bianchi, F.; Bottazzi, M.; Careri, M.; Musci, M. Chromatographia 2004, 60, 323.
8. Heintz, A. M.; Duffy, D. J.; Hsu, S. L.; Suen, W.; Chu, W.; Paul, C. W. Macromolecules 2003, 36, 2695.
9. Seo, W. J.; Jung, H. C.; Hyun, J. C.; Kim, W. N.; Lee, Y. B.; Choe, K. H.; Kim, S. B. J Appl Polym Sci 2003, 90, 12.
10. Lim, H.; Kim, S. H.; Kim, B. K. Polym Adv Technol 2008, 19, 1729.
11. Lim, H.; Kim, S. H.; Kim, B. K. J Appl Polym Sci 2008, 110, 49.
12. Lim, H.; Kim, S. H.; Kim, B. K. Macromol Res 2008, 16, 467.
13. Lim, H.; Kim, S. H.; Kim, B. K. Polym Eng Sci 2008, 48, 1518.
14. Kim, S. H.; Lim, H.; Song, J. C.; Kim, B. K. J Macromol Sci Pure Appl Chem 2008, 45, 323.
15. Saha, M. C.; Kabir, M. D. E.; Jeelani, S. Mater Sci Eng A 2007, 479, 213.
16. Seo, W. J.; Sung, Y. T.; Han, S. J.; Kim, Y. H.; Ryu, O. H.; Lee, H. S.; Kim, W. N. J Appl Polym Sci 2006, 101, 2879.
17. Harikrishnan, G.; Patro, T. U.; Khakhar, D. V. Ind Eng Chem Res 2006, 45, 7126.
18. Harikrishnana, G. T.; Umasankar, P.; Khakhar, D. V. Carbon 2007, 45, 531.
19. Her, K.; Lim, S.; Kim, D. Korean Chem Eng Res 2009, 47, 208.
20. Seo, W. J.; Sung, Y. T.; Kim, S. B.; Lee, Y. B.; Choe, K. H.; Choe, S. H.; Sung, J. Y.; Kim, W. N. J Appl Polym Sci 2006, 102, 3764.
21. Rehab, A.; Akelah, A.; Agag, T.; Betiha, M. J Appl Polym Sci 2007, 106, 3502.
22. Nanoclay Available at http://www.nanoclay.com accessed on 20 March 2009.
23. Seo, W. J.; Park, J. H.; Sung, Y. T.; Hwang, D. H.; Kim, W. N.; Lee, H. S. J Appl Polym Sci 2004, 93, 2334.
24. Xu, Z.; Tang, X.; Gu, A.; Fang, Z. J Appl Polym Sci 2007, 106, 439.
25. Singh, H.; Sharma, T. P.; Jain, A. K. J Appl Polym Sci 2007, 106, 1014.
26. Oertel, G. Polyurethane Handbook; Hanser Publishers: New York, 1985.
27. Szycher, M. Szycher's Handbook of Polyurethanes; CRC Press: New York, 1999.
28. Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. Transport Phenomena; Wiley: New York, 2006.