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Preparation and Properties of Polydimethylsiloxane-Mica Composites

Zhenmei Jia, Shuangjun Chen, Jun Zhang
Department of Polymer Science and Engineering, College of Materials Science and Engineering,
Nanjing University of Technology, Nanjing 210009, People's Republic of China
Correspondence to: J. Zhang (E-mail: zhangjun@njut.edu.cn)

ABSTRACT: This is a comparison study of the effects of various colloids on polydimethylsiloxane (PDMS) nanocomposites. Mica of layered structure and silica of nanospherical shape were both used with different content. Silane coupling agent was used for surface modification of mica to improve its dispersion. Wide X-ray diffraction patterns showed no intercalation during the incorporation of mica into PDMS matrix. Rheological characterization of the PDMS composites before curing showed that viscosities of PDMS-mica composites were much lower than that of PDMS composites with silica, particularly at low shear rates. Scanning electron microscope (SEM) suggested the existence of mica lamellar structure with high aspect ratio within the PDMS matrix. After vulcanization at room temperature, PDMS-mica composites could obtain mechanical properties close to that of PDMS composites with silica at same filler content. The cooperative effects of mica with silica showed that same mechanical properties of PDMS composites could be obtained at much lower viscosity, cost, and processing insecurity. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

The utilizations of silicone elastomers spread almost every field of the society and endue a variety of commercial products, such as dental copings,[1] soft contact lenses,[2] and a variety of electric and electronics applications, e.g., coatings for porcelain and glass insulators,[3] dielectric elastomers,[4] sealants[5] due to their incomparable properties, such as high thermal resistance, low temperature flexibility, outstanding dielectric properties, biological inertia, and water repellency. However, the unfilled silicone elastomers usually have relative low mechanical properties, resulting in no practical application. The most widely used fillers in silicone elastomers are silica and carbon black with nanosize and spherical shape.[6] Because of the extreme interaction of polymer and these fillers, polymers are effectively reinforced. However, huge increase in viscosity and poor dispersibility are also brought out when the large amount of fillers are incorporated into polymer matrix.

Layered silicates with dimensions in two directions larger than that in the third are expected to give superior two dimensional reinforcements on a small addition.[7] Theoretical works have also shown that the addition of materials with a sufficiently large aspect ratio can significantly enhance the mechanical strength of a composite.[8] As one of layered silicate clays, mica has attracted attentions because the aspect ratio of mica layers greatly exceeds that of smectites.[9] Osman et al. investigated reinforcement of PDMS networks by mica flakes and the results indicated that mica platelets increased the elastic modulus of PDMS networks dramatically and were much superior to glass spheres with similar diameter, although the polymer chains did not intercalate the aluminosilicate layer of mica.[10] Indeed, PDMS-mica composites should be paid more attention because of their gain of both fluidity and reinforcement.

Although the mechanical strengths of room temperature vulcanized (RTV) rubbers are generally lower than those of the corresponding heat-cured silicones, for many applications, their convenience especially the fluidity outweighs their reduced mechanical properties.[11–16] In this article, we mainly focused on the rheological and mechanical properties of addition-type RTV PDMS and mica hybrid composites. A silane coupling agent was used to improve dispersion of pristine mica in polymer matrix. For comparison, rheological and mechanical properties of PDMS were investigated by varying amounts of mica and silica. A combination of wide angle X-ray diffraction (WAXD), scanning electron microscope (SEM) were used to demonstrate dispersion states of mica and precipitated silica in polymer matrix and the interaction between filler particles and polymer matrix.

Table I. Components in Mica by XRF Spectrometry

Composition	wt %	Standard error	Element	wt %	Standard error
SiO_2	47.91	0.25	Si	22.40	0.12
Al_2O_3	34.63	0.24	Al	18.33	0.13
K_2O	10.30	0.15	K	8.55	0.13
Fe_2O_3	4.85	0.11	Fe	3.40	0.08
Na_2O	0.69	0.034	Na	0.51	0.026
MgO	0.67	0.033	Mg	0.40	0.020
TiO_2	0.62	0.031	Ti	0.37	0.019
Others	0.33	-	Others	-	-

EXPERIMENTAL

Materials

Vinyl-terminated PDMS (DY401, η_{25} = 1.5 Pa·s, 0.52 wt % vinyl denoted by the supplier), vinyl-branched PDMS (DY411, η_{25} = 4.8 Pa·s, 1.80 wt % vinyl) and hydrogen-containing silicone oil used as a crosslinking agent were purchased from Dayi (Shangdong, China). Platinum complex (homemade, 0.24 wt % Pt) was prepared in the laboratory according to literature.[17] Muscovite mica used for this study was supplied by Chuzhou Grea Mineals (Anhui, China), and the average particle size was 4.2 μm. Precipitated silica, modified by hexamethyldisilazane, was purchased from Wanzai Chemical (Jiangxi, China) and the particle size was 30–100 nm. The silane coupling agent was γ-methacryloxypropyltrimethoxysilane (KH-570) and used as received.

Sample Preparation

Silane coupling agent KH-570 (1 wt % ratio of mica) was used to modify the mica surface with ethanol as a dispersant. After stirred for 30 min at 60°C, the mixture was evaporated at negative pressure to remove ethanol. For estimating the interaction between the mica and silane coupling agent KH-570, extraction experiment was performed as follows: modified mica was wrapped with a filter paper and put into a Soxhlet extractor. Acetone was used as a solvent and fluxed through the sample for 24 h at 70°C. After the extraction, sample was dried in a vacuum desiccator at 70°C to constant weight.

Blends of vinyl-terminated and vinyl-branched PDMS (mass ratio = 100 : 15) were used as precursor. The content of the mica (or silica) was varied from 5 to 50 parts per hundred of PDMS (abbreviated as phr). The mixing was conducted as follows: (1) Mixtures were ground with a three-roll mill (ST65/150, Changzhou Zili, China) at room temperature for three times; (2) Appropriate hydrogen-containing silicone oil (the weight ratio of hydrogen in hydrogen-containing silicone oil to vinyl in PDMS blends is 1.3) and platinum catalyst (20 ppm Pt of the total sample weight) were added to the mixtures and stirred; (3) The mixtures were poured into a polytetrafluoroethylene mold after eliminating the air bubble and cured at room temperature for about 8 h.

Characterization

X-ray fluorescence (XRF) spectrometry was done in an ADVANT XP Thermo (Electron's ARL, Switzerland), to analysis the components of the mica. The components of mica is characterized by XRF spectrometry in Table I, in which mica is composed of 22.40 wt % Si, 18.33 wt % Al, 8.55 wt % K, 3.40 wt % Fe and trace amounts of Na, Mg, Ti. Containing 8.55 wt % K^+, this material can be classified into the potassium-rich mica, which do not expand in water.

Rheology experiments were conducted on a HAAKE Rheo-Stress 600 instrument. Steady shear measurements from 0.1 to 100 s^{-1} were conducted by using a set of 35 mm diameter parallel plates with a sample thickness of ca. 0.7–0.9 mm.

To characterize the phases in detail, wide angle X-ray diffraction was done in an XRD-6000 diffractometer, (Shimadzu, Japan), using Cu K_α radiation at 40 kV and 30 mA. The scanning angle 2θ ranged from 1.7 to 60° with the scanning velocity of 4°/min.

Surface morphology was observed in a JSM-5610LV SEM (JEOL, Japan) with an accelerating voltage of 15 kV. Samples for the SEM were fractured in liquid nitrogen and coated with a thin layer of gold.

The samples were manufactured as standard dumbbell pieces and measured by MZ-2000C electronic pulling tester (Shenzhen Sans Test Machine, China), with an extension rate of 500 mm/min at room temperature, according to ISO 37-1994. Shore A hardness was recorded according to ISO 868. Viscosity was measured according to ASTM D 1084-1998.

RESULTS AND DISCUSSION

Figure 1 shows the SEM image of pristine mica. Mica is monoclinic with spatial structure: a sheet of alumina octahedral connects to two sheets of silicone-oxygen tetrahedral, such as a "sandwich". The isomorphic substitution of the tetrahedral or octahedral cations, e.g., the substitution of Al^{3+} with Mg^{2+} or Na^+, generates negative charges that are counterbalanced by potassium (K^+) located inside the galleries. These ions are hard to exchange because they are strongly bounded to interlayer surfaces by inner-sphere complexes.[18] From Figure 1, average diametric size of mica flake was about 4 μm, and the average thickness was about 0.15 μm. The radius- thickness ratio was almost 26. The invariant interlayer spacing is confirmed by the latter WAXD results.

Extraction experiment combining with FTIR tests (not shown) indicates that the silane coupling agent KH-570 is reacted with mica by chemical bonding.[19] Scheme 1 presents the surface modification of mica using silane coupling agent. Silane

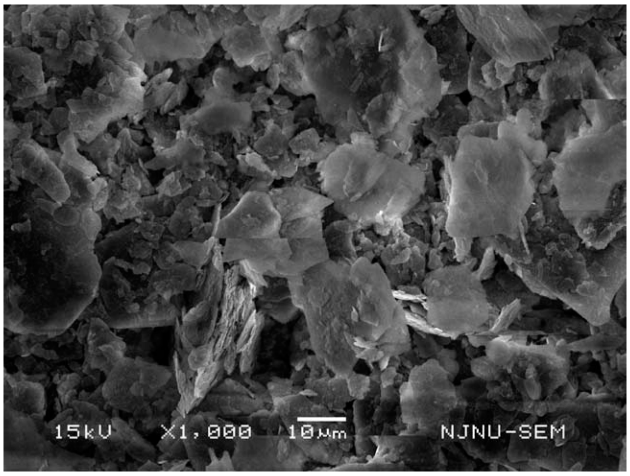
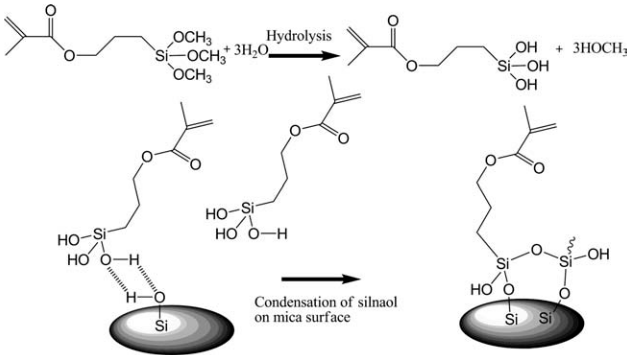


Figure 1. SEM image of pristine mica.

coupling agent is first hydrolyzed to be silanol, which can be of condensation with the silanol of mica surface. The WAXD patterns of pristine mica and surface modified mica are shown in Figure 2. The WAXD pattern of pristine mica shows characteristic peaks at $2\theta = 9.0$, 17.9, 26.9°, and 36.0°, which are assigned to the (001), (002), (003), and (004) basal reflection respectively.[10] After treated with 1 wt % content of silane coupling agent, there are four peaks with the same position in the WAXD pattern. This means that layer spacing of the KH-570 treated mica does not increase after surface bonding with silane coupling agent.[20,21]

For room temperature vulcanized vinyl PDMS elastomers, viscosity of fluid is very important for its processing procedure. The viscosity of polymer/filler system is influenced by many factors, including the rheological behavior of polymer matrix, particle characteristics (size, distribution, and content), dispersed state, interaction between particles, and interaction between particles and polymer matrix.[22] Before hydrosilylation reaction with hydrogen-containing silicone oil, rheology properties of PDMS and filler mixed composites were tested by rotation viscometer. Figure 3 gives logarithmic plots of the steady state shear viscosity of PDMS composites containing different amounts of mica and precipitated silica vs. shear rate at room temperature 25°C. The shear rate ranges from 0.1 to 100 s^{-1}.



Scheme 1. Hydrolysis reaction of silane coupling agent of KH-570.

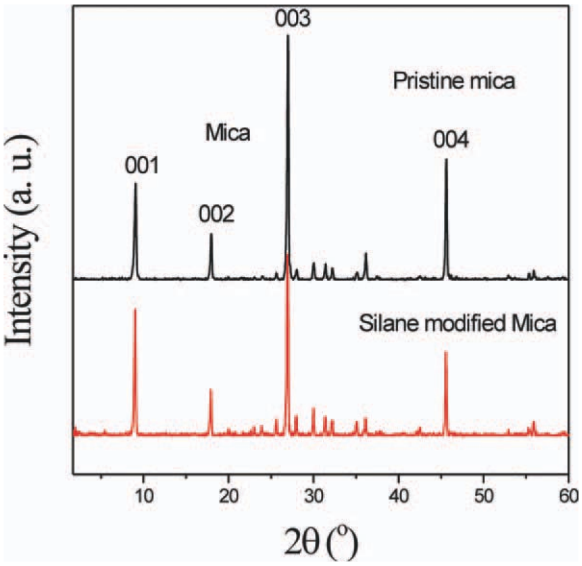


Figure 2. WAXD patterns of pristine mica and KH-570-treated mica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As shown in Figure 3, the viscosity of PDMS precursor almost keeps stable at about 2.1 Pa·s as shear rate increasing from 0.1 to 100 s^{-1}. However, as silica or mica is incorporated into PDMS, inspection of Figure 3(A,B) reveals a significant difference between these two PDMS composites, particularly at low shear rates. As known, primary particle size of precipitated silica used in this experiment is in the nanoscale with large specific surface area. The strong interaction between the PDMS and silica makes the silica nanoparticles act as physical crosslinked points, which cannot be untied at low shear rates. When shear rate increases, very obvious shear thinning occurs for PDMS and 20 or 25 phr silica composites in Figure 3(A). Mica is hard

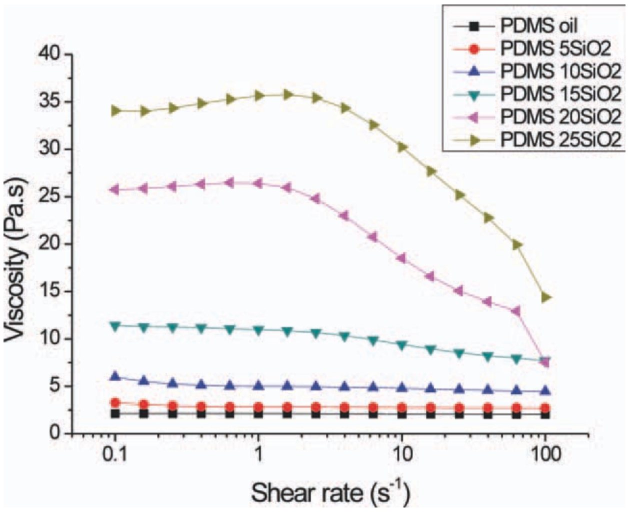
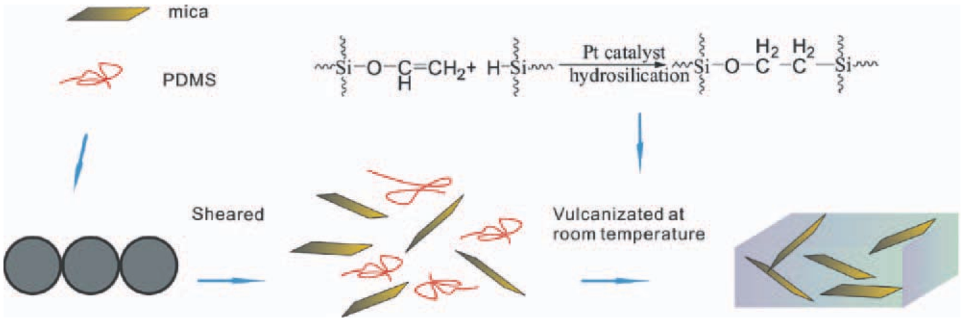


Figure 3. Viscosity of PDMS matrix filled with different content of (A) precipitated silica and (B) mica; and (C) viscosity vs. filler content at shear rate 1 and 100 s^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Hydrosilylation of vinyl-terminated polysiloxane oil and hydrogen-containing silicone oil catalyzed by platinum complex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to be intercalated or exfoliated. However, PDMS-mica composites also show shear thinning, indicating that there exits interaction between the PDMS chains and mica flakes. In Figure 3(C), with the increasing amounts of these two fillers, the viscosity of the PDMS increases respectively. Obviously, the viscosity of PDMS filled with precipitated silica increases much more than that of PDMS filled with mica. For example, the viscosity of PDMS mixed with 50 phr mica at shear rate 1 s^{-1} is 6.69 Pa·s, while that filled with 25 phr precipitated silica is almost five times, 35.66 Pa·s. At the shear rate 100 s^{-1}, the viscosity of PDMS mixed with 50 phr mica is 5.12 Pa·s, not changed much. But that filled with 25 phr precipitated silica is decreased sharply to 14.4 Pa·s.

Scheme 2 presents the preparation procedures of PDMS-mica hybrid composites. By using low molecular weight hydrogen-containing silicone oil as a crosslinker and platinum complex as a catalyst, crosslinking reaction can be accomplished through a hydrosilylation reaction that Si—H group was reacted with vinyl group. The network structures were formed after 8 h at room temperature.[23,24] In order to avoid the side reaction and make the reagents fully react, the weight ratio of hydrogen in hydrogen-containing silicone oil to vinyl in PDMS blends is 1.3/1. However, in the real hybrid composites, the active groups on the fillers' surface also act as physical or chemical crosslinking points which play role in the formation of network structure.

The WAXD patterns of PDMS matrix containing different amounts of mica are shown in Figure 4. There are four peaks with the same position in the WAXD spectrum which indicates that the crystal form of mica is not changed by the vulcanization process. However, intensity of the (001) reflection increases more rapidly, (003) reflection decreases with the content of 50 phr mica compared with the pattern of pristine mica. Moreover, the intensities of all peaks become weak containing 5–35 phr mica, even at containing 5 and 10 phr mica there is no peak appeared basically. The invariant 2θ value of hybrids primary peaks indicates that the interlayer spacing of mica keeps invariant and the lattice structure of mica is influenced by the polymer chain or the manufacturing process. Debnath et al.[25] has mentioned that breakdown of mica particles during mixing and processing caused reduction of aspect ratio. In our experiment, mixtures were ground with a three-roll mill. From these points, the ratios of I_{001}/I_{003} (I_{001} stands for the intensity of mica 001 basal reflection, I_{003} stands for the intensity of mica 003 basal reflection) variation in Figure 4 (50 phr mica, $I_{001}/I_{003} = 1.20$) compared to Figure 1 (pristine mica, $I_{001}/I_{003} = 0.39$) can be ascribed to the reduction of aspect ratio in processing.

Figure 5 gives the SEM images of break surfaces of PDMS composites filled with different content of mica. From the image of pristine mica (Figure 1), we can obviously observe a flake-like morphology and typical lamellar structures with high aspect ratio (lateral length/thickness), which is a key influence on the improvement of mechanical performance.[25,26] Figure 5(A–F) shows fracture surfaces images of the PDMS containing 5–50 phr mica respectively. In all of these figures, it is observed that the typical lamellar structures of mica. Mica is dispersed homogeneously in the polymer matrix at the low concentration and there exist obvious lamellar structure. However, careful inspection of these fracture surfaces indicates that the dispersion of silane-treated mica in PDMS matrix decreases with the increasing mica content. In Figure 5(F), for 50 phr mica-filled PDMS, there exists obvious aggregation of particles. Figure 6(A–D) shows the images of PDMS matrix filled with 5–25 phr

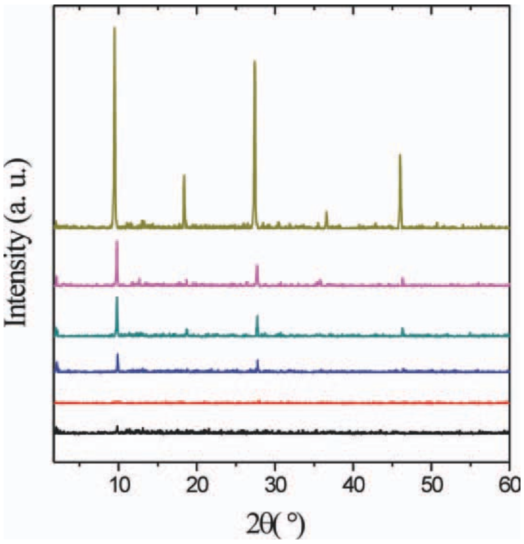


Figure 4. WAXD patterns of PDMS composites containing different content of mica (from down to up: 5, 10, 20, 25, 35, and 50 phr). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

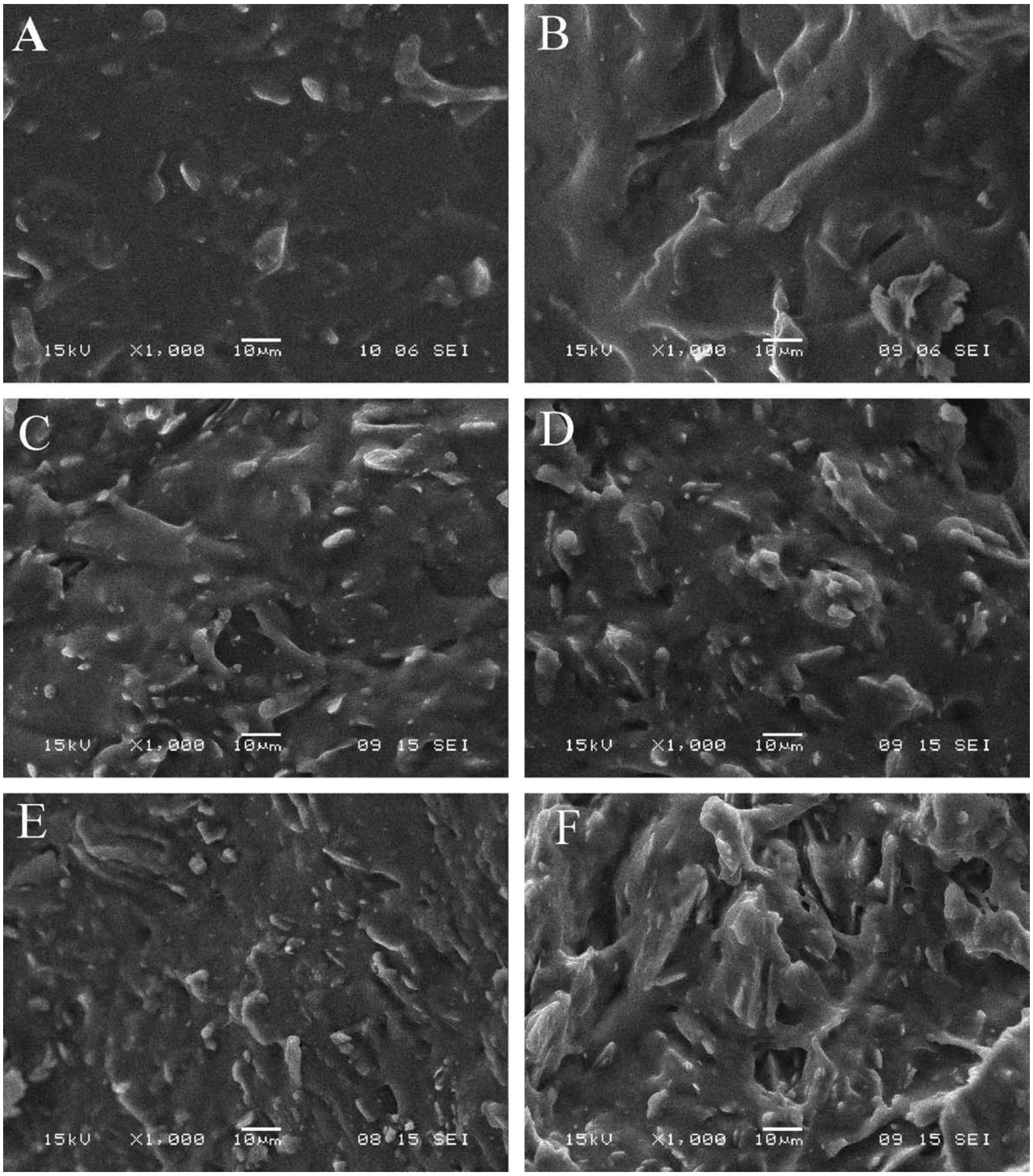


Figure 5. SEM images of PDMS filled with different amounts of mica: A-5phr, B-10phr, C-20phr, D-25phr, E-35phr, F-50phr.

precipitated silica. These samples were also fractured in liquid nitrogen for SEM observation. By loading precipitated silica [Figure 6(A–D)], very little aggregation of silica appears in the PDMS composites, and the interfacial region between silica and PDMS matrix is ambiguous. However, at the addition of 25 phr precipitated silica [Figure 6(E)], the aggregation becomes obvious in the PDMS matrix. Even so, the dispersion state of precipitated silica was much better than that of mica. From the SEM images of PDMS filled with mica and precipitated silica, the much better dispersion of precipitated silica is corresponding for the much higher viscosity of PDMS silica composites than that of mica.[27]

It is difficult to understand the mechanism by which fillers influence the properties of the rubber, because the number of variables involved in the experiments is large and some of them are hard to control. The particle size and shape, the condition of the particle surface, and the degree and type of cure are a few examples. Better reforcement is usually achieved by increasing the surface area of the filler, which increases the interaction between the filler and PDMS.[10] The morphology of the composites is often considered to be of crucial importance for the mechanical properties. Figure 7 gives the plots of mechanical properties of silicone rubber versus filler contents. Improvement in tensile strength compared to unfilled PDMS matrix is shown in

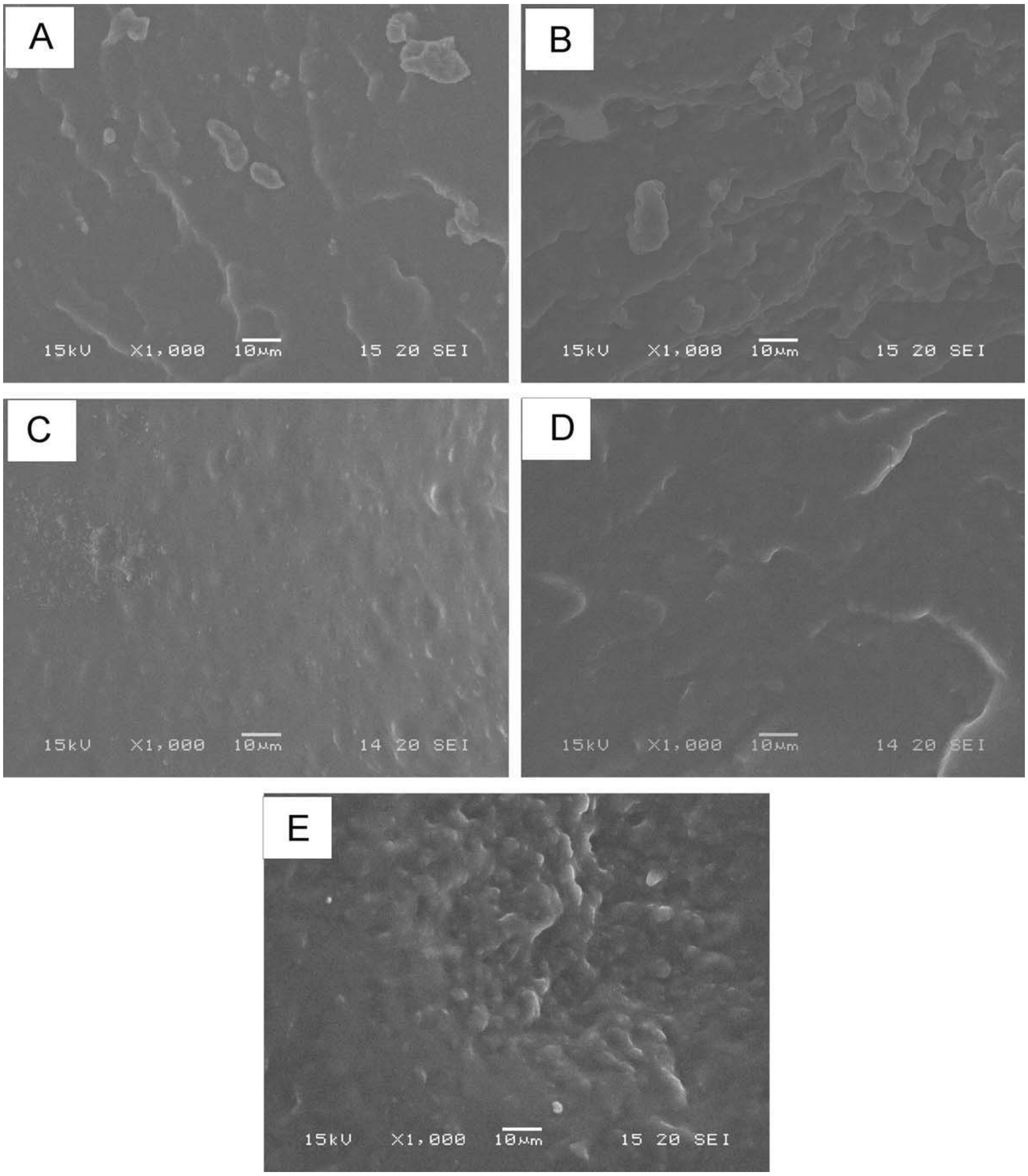


Figure 6. SEM images of PDMS filled with different amounts of precipitated silica: A-5phr, B-10phr, C-15phr, D-20phr, E-25phr.

Figure 7(A). It is noted that there appears the same increasing tendency in tensile strength, no matter SiO_2 or mica. The tensile strength of PDMS filled with 50 phr mica is 2.0 MPa, which is close to that filled with 20 phr precipitated silica. In Figure 7(B), the elongation at break of PDMS filled with precipitated silica increases and then decreases as the filler contents increase. It achieves a maximum of about 288% at the precipitated silica loading of 15 phr. However, the elongation at break of PDMS/mica composite decreases from 230 to 100% as the mica content ranges from 0 to 50 phr. Suggested by SEM images in Figures 5 and 6, mica and silica are both dispersed homogeneously in the polymer matrix at the low concentration. There exist some obvious micro-caves in PDMS-mica composites when mica content increase, which is due to overlapping of the lamellar structure with high aspect ratio. Along with increasing content of mica, the overlapping of layered structure of mica can provide a supporting skeleton during the tensile process. However, the decreasing dispersion of mica observed by SEM also causes a decrease in elongation at break. In Figure 7(C), hardness (Shore A) of silicone rubber increases with filler amounts.[27] From Figure 3, the viscosity of PDMS filled with 20 phr precipitated silica is much higher than that of filling with 50 phr mica at low shear rate. In a word, combining the results of mechanical properties and viscosity, mica could be a very good

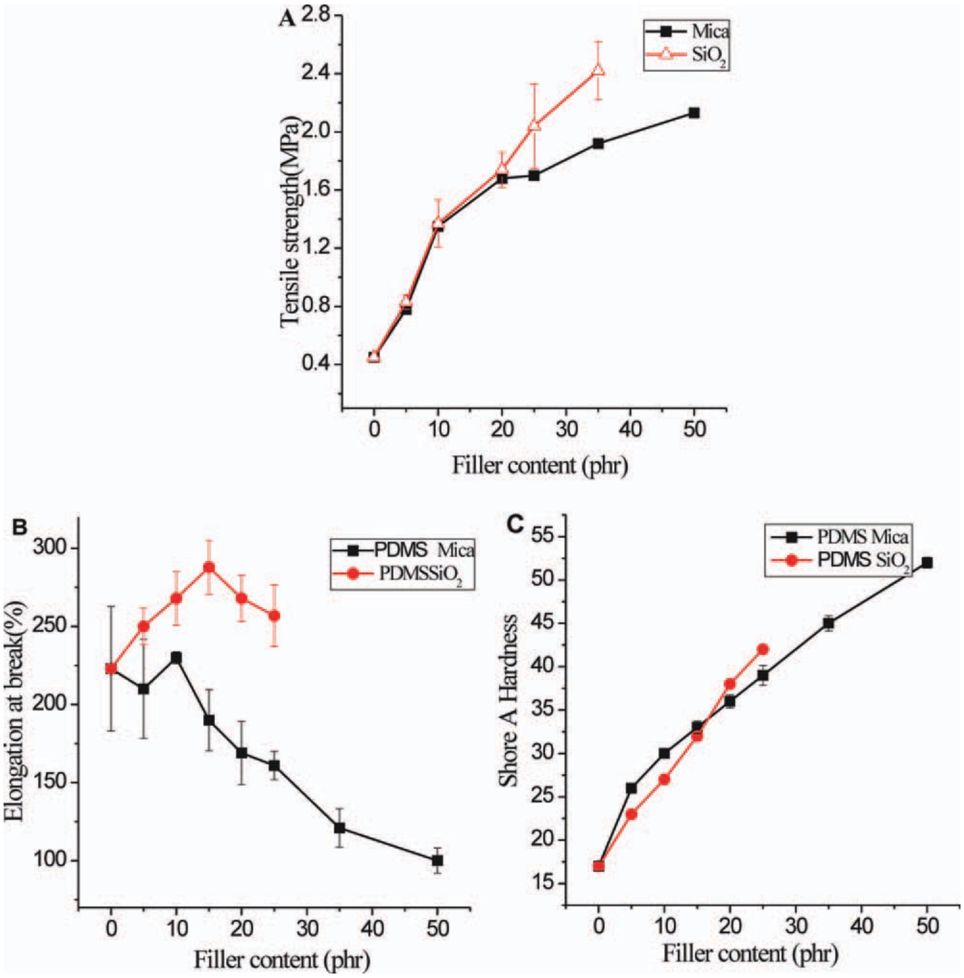


Figure 7. Mechanical properties of PDMS matrix filled with different content of mica and precipitated silica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

commodity compared with precipitated silica, because mica brings low viscosity in same mechanical properties.

Table II exhibits the results of mechanical properties and viscosity of PDMS containing mica and precipitated silica at different proportions with the same total content. In Table II, tensile strength, elongation at break and viscosity increase as the precipitated silica increases, while hardness of the hybrids changes little. For mica/precipitated silica PDMS system, the tensile strength, elongation at break and the viscosity of composites increase with increasing amounts of precipitated silica. The tensile strength increases from 1.99 to 2.65 MPa, elongation at break from 145 to 233%, viscosity from 3.8 to 45.5 Pa·s, respectively. It is valuable to be noted that the component of mica/silica = 20/10 phr, of which the tensile strength is 2.56 MPa, the elongation at break is 181%, Shore A hardness is 43 and the viscosity at 1 s^{-1} is only 8.9 Pa·s. In contrast, the relative data of PDMS with 25 phr silica are 2.42 MPa of tensile strength, 257% of elongation at break, 42 of Shore A hardness, and 35.65 Pa·s of the viscosity at 1 s^{-1}. Figure 8(A–C) present the SEM images of PDMS composites loaded with total 30 phr fillers with different ratios of mica/silica. Observed from Figure 8, there exist both layered structures and spherical shapes of fillers. As the mica ratio of the fillers decreases, the interface in the images become clear, which means the aggregation of mica particles, inducing the decline of the elongation at break. There are mostly none micro-caves in the image in Figure 8(A) suggesting

Table II. Mechanical Properties of PDMS Filled with Mica and Precipitated Silica at Different Proportions

$Mica/SiO_2$ (phr/phr)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)	Viscosity (mPa·s)
30/0	1.99	145	46	6400
20/10	2.56	181	43	19,000
15/15	2.64	193	46	41,000
10/20	2.65	233	46	64,000
0/30[a]	2.46	234	44	91,000

[a] There are defects in the sample because of the existed bubbles for the high viscosity.

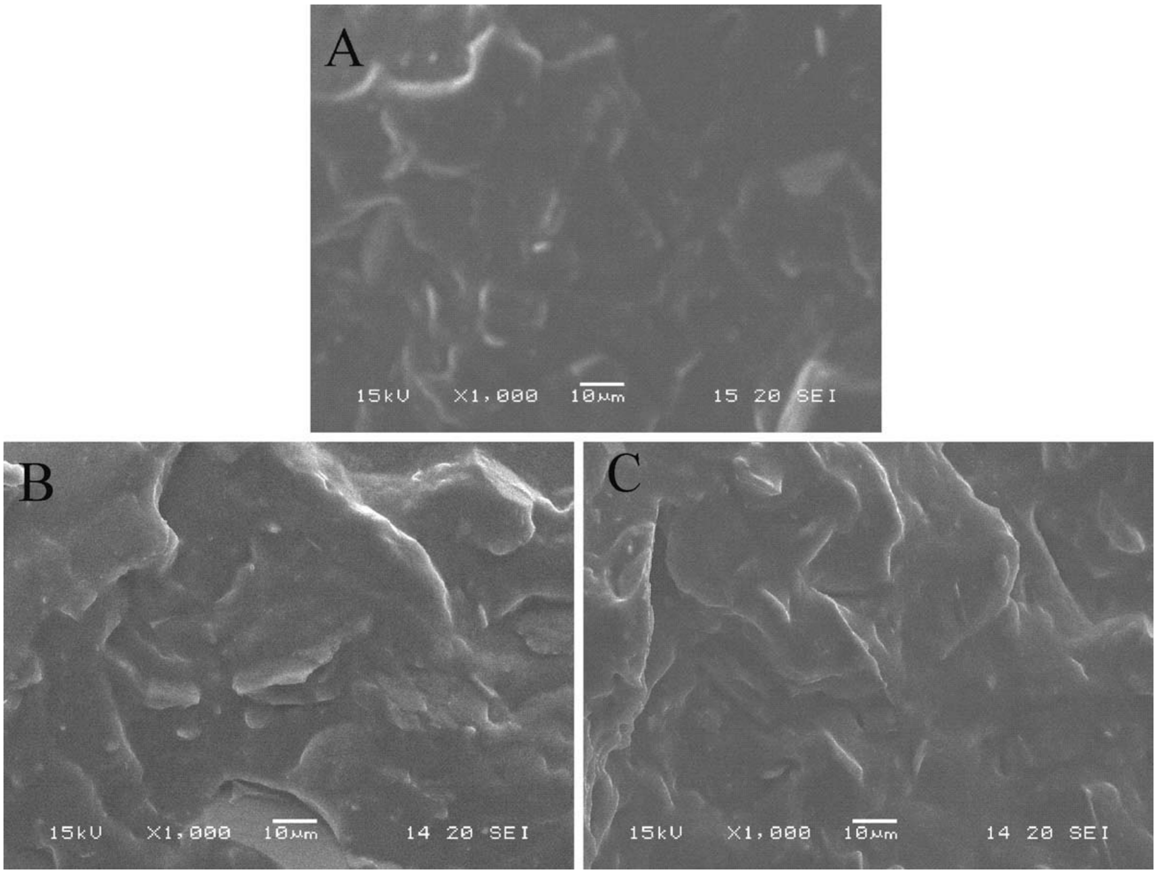


Figure 8. SEM images of PDMS filled with different content of mica and precipitated silica: A-10phr/20phr, B-15phr/15phr, C-20phr/10phr.

the good dispersion, and also the corporation between layered structures and spherical shapes of fillers both give the composites an optimized mechanical and rheological properties.

As known, the pristine mica is very low of cost. In a word, by cooperating mica with silica, same mechanical properties of PDMS composites could be obtained at much lower viscosity, cost, and processing insecurity, for example, the pneumonokoniosis which often occurs during the processing procedure of the silica.

CONCLUSIONS

In this study, low cost mica was effectively incorporated into RTV silicone rubber with low viscosity and good reinforcement. Silane coupling agent KH-570 was used to improve the dispersibility of mica in PDMS matrix. With the same tensile strength, the viscosity of polymer filled with mica was dramatically lower than that filled with precipitated silica. SEM suggested the existence of mica lamellar structure and aggregates of precipitated silica within the PDMS matrix. The reinforcement of silicone rubber from the mica might be due to the existence of the lamellar structure with high aspect ratio. The WAXD patterns of silicone rubber containing different amounts of mica indicated that PDMS did not intercalate into mica interlayer. By cooperating mica with silica, same mechanical properties of PDMS composites could be obtained at much lower viscosity, cost and processing insecurity.

REFERENCES

1. Haggblad, H.-A.; Hockauf, M.; Eriksson, M.; Berggren, C. *Powder Technol.* **2005,** *154*, 33.
2. Dupas-Bruzek, C.; Robbe, O.; Addad, A.; Turrell, S.; Derozier, D. *Appl. Surf. Sci.* **2009,** *255*, 8715.
3. Cai, D. K.; Wen, X. S.; Lan, W., Yu, J. H. *IEEE* **2004,** *2*, 800.
4. Razzaghi-Kashani, M.; Gharavi, N.; Javadi, S. *Smart Mater. Struct.* **2008,** *17*, 065035/065026-065035/065035.
5. Xu, X. M.; Song, Y. H.; Zheng, Q.; Hu, G. H. *J. Appl. Polym. Sci.* **2007,** *103*, 2027.
6. Wang, S.; Long, C.; Wang, X.; Li, Q.; Qi, Z. *J. Appl. Polym. Sci.* **1998,** *69*, 1557.
7. Mack, J. J.; Viculis, L. M.; Ali, A.; Luoh, R.; Yang, G. L.; Hahn, H. T.; Ko, F. K.; Kaner, R. B. *Adv. Mater.* **2005,** *17*, 77.
8. Alexandre, M.; Dubois, P. *Mater. Sci. Eng. R* **2000,** *28*, 1.
9. Tamura, K.; Yokoyama, S.; Pascua, C. S.; Yamada, H. *Chem. Mater.* **2008,** *20*, 2242.
10. Osman, M. A.; Atallah, A.; Mler, M.; Suter, U. W. *Polymer* **2001,** *42*, 6545.
11. Lund, K. H.; Petersen, J. H. *Eur. Food Res. Technol.* **2002,** *214*, 429.
12. Kobayakawa, S. J.; Bradley, D.; Gilmore, M. S. *Curr. Eye. Res.* **2005,** *30*, 741.

13. Dolezel, B.; Adamirova, L.; Vondracek, P.; Naprstek, Z. *Biomaterials* **1989,** *10*, 387.
14. Michael, A. B. *Biomaterials* **2006,** *27*, 3274.
15. Noll, W. J.Chemistry and Technology of Silicones; Academic Press: New York, **1968.**
16. Clarson, S. J.; Semlyen, J. A.Siloxane Polymer; PTR Prentice Hall: New Jersey, **1993.**
17. Karstedt, B. D. U.S. Pat. 3,715,334 (1973).
18. Tamura, K.; Yokoyama, S.; Pascua, C. S.; Yamada, H. *Chem. Mater.* **2008,** *20*, 2242.
19. Gao, H. M.; Yuan, J. Z.; Wang, X. R.; Guan, J. F.; Zhang, L. Y.; Jing, Z. Q.; Mao, Y. L. *J Wuhan Univ. Technol. Mater. Sci. Ed.* **2007,** *22*, 470.
20. Negrete, N. N.; Letoffe, J.-M.; Putaux, J.-L.; David, L.; Bourgeat-Lami, E. *Langmuir* **2004,** *20*, 1564.
21. Isoda, K.; Kuroda, K.; Ogawa, M. *Chem. Mater.* **2000,** *12*, 1702.
22. Xu, X. M.; Gao, C. H.; Zheng, Q. *Polym. Eng. Sci.* **2008,** *48*, 656.
23. Gussoni, M.; Greco, F.; Mapelli, M.; Vezzoli, A.; Ranucci, E.; Ferruti, P.; Zetta, L. *Macromolecules* **2002,** *35*, 1722.
24. Esteves, A. C. C.; Brokken-Zijp, J.; Laven, J.; Huinink, H. P.; Reuvers, N. J. W.; Van, M. P.; With, G. *de. Polymer* **2009,** *50*, 3955.
25. Debnath, S.; De, S. K.; Khastgir, D. *J. Mater. Sci.* **1987,** *22*, 4453.
26. Shelly, D.B.; Emmanuel, P. G. *J. Polym. Sci. Part B: Polym. Phys.* **2000,** *38*, 1595.
27. Labruyere, C.; Monteverde, F.; Alexandre, M.; Dubois, P. *J. Nanosci. Nanotechnol.* **2009,** *9*, 2731.
28. Seema, A.; Justin, M. V.; Dayas, K. R. *Polym. Adv. Technol.* **2009,** *20*, 459.