

# Effect of Coprecipitated Barium Ferrite on the Cure Characteristics and Dynamic Properties of Natural Rubber–Ferrite Composites Around Percolation

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**ABSTRACT:** The influence of coprecipitated hexagonal barium ferrite BaFe<sub>12</sub>O<sub>19</sub> phase on the cure characteristics and dynamic properties of natural rubber–ferrite composites has been studied as a function of ferrite loading up to 220 phr (part per hundred part of rubber). Unusual characteristics of coprecipitated ferrite particles were discovered by scanning electron microscope. The results show that scorch time  $t_{10}$  and cure time  $t_{90}$  decrease dramatically with increasing ferrite content up to critical ferrite loading. After 160 phr,  $t_{90}$  increases sharply with increasing ferrite content, in contrast to saturation of  $t_{10}$ . Minimum torque recorded normal behav-

ior at low ferrite loading, whereas it decreases with increasing ferrite content at high ferrite loading because of dilution effects. The storage modulus  $E'$  and loss modulus  $E''$  decrease with increasing temperature. The loss tangents ( $\tan\delta$ ) of the composites are greater than those of the pure rubber. Linear viscoelastic behavior was observed as a result of the homogeneity and compatibility of the composites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3294–3299, 2009

**Key words:** rubber ferrite composites; dynamic properties; cure characteristics; barium ferrite

## INTRODUCTION

Hard ferrite or ceramic permanent magnets are considered to be an important and sophisticated class of engineering materials, which are used extensively in various applications. Hexaferrite magnets have found acceptance in many electronic products, as a result of their superior cost efficiency, large coercivity, and specific magnetic saturation associated with their high magnetic and chemical stability.<sup>1,2</sup> Many sintered magnets are brittle, hard, and difficult to machine to their final form. The advantages of polymer-bonded magnets over their metallic and ceramic counterparts include low weight, resistance to corrosion, ease of machining and forming, and capability for high production rates.<sup>3</sup>

The evaluation of the cure characteristics and dynamic properties helps to understand the processability and also provides valuable information about the matrix–filler interaction, percolation threshold, and filler dispersion. These essential characteristics play an important role in determining the overall physical properties of the composites. Furthermore,

the filler parameters influence the dynamic and the physical properties of the composites in different ways.<sup>4</sup> For example, (i) particle–particle interactions become important above certain volume fractions, depending on the particle morphology.<sup>5,6</sup> (ii) The percolation limit can be achieved at different filler loadings, depending on the aspect ratio and the particle size of the fillers.<sup>7,8</sup> (iii) Filler aggregation, especially at high loading, leads to chain-like filler structure or clusters, which affect rubber properties and viscoelastic behavior.<sup>4</sup> (iv) Filler increases the thermal conductivity of the composite matrix, consequently reducing the cure time for thick rubber articles and giving uniform curing throughout the material.<sup>9</sup> In other words, the dynamic properties of rubber products are influenced by many factors, such as the size, shape, nature, and state of distribution of filler; type of rubber; adhesion and thermal compatibility of the matrix; and so forth.<sup>10,11</sup> Thus, the overall effect of each of the variables on the final properties of the composites is complex.

A few researchers have reported the processing and dynamic properties of polymer composites containing hexaferrite prepared by ordinary powdered methods up to ferrite loading of 120 phr (part per hundred part of rubber). The result indicates poor adhesion between ferrite particles and polymer, despite the fact that the percolation threshold was not

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achieved yet for these types of composites. The maximum loading was about 120 phr.<sup>12-15</sup>

Therefore, the current study aims to investigate the compatibility of barium ferrite (BaF)-natural rubber (NR) composites (RFCs) with increasing coprecipitated ferrite particles loading to the percolation limit. We have previously reported dynamic mechanical properties for BaF-NR composites up to 120 phr ferrite loading.<sup>16</sup> The RFCs having a rather low density, high coercivity, large stored energy, and high flexibility were successfully produced. In addition, the results showed that tensile strength, strain at break and modules are highly influenced by the size, shape, and volume fraction of the ferrite particles. These promising data encouraged us to increase the ferrite loading in rubber matrix. In the current research, ferrite loading was increased from 140 to 220 in steps of 20. Cure characteristics and dynamic properties of these composites were determined and presented here.

## EXPERIMENTAL

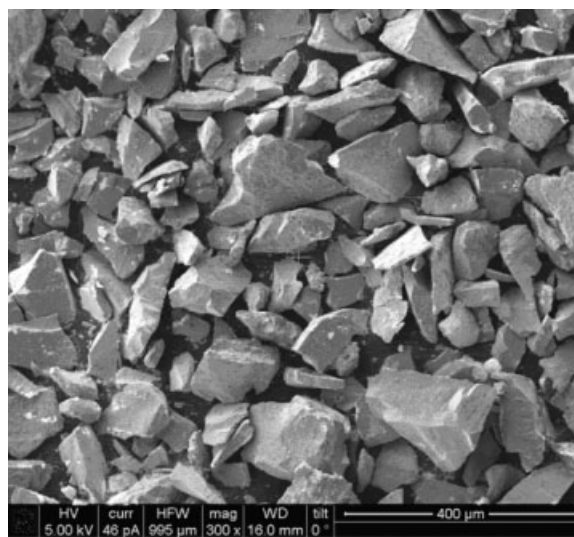
### Materials

Hexagonal barium ferrite  $\text{BaFe}_{12}\text{O}_{19}$  phase was prepared by coprecipitation method according to Makled et al.<sup>17</sup> Powder having a coercive force 5 kOe, saturation magnetization 65.5 emu/g, and 45–200  $\mu\text{m}$  particle size was selected to mix with smoked rubber sheet. The recipe and mixing procedures were reported in previous research.<sup>16</sup>

### Techniques

The cure characteristics, scorch time ( $t_{10}$ ), cure time ( $t_{90}$ ), minimum torque (ML), and maximum torque of RFCs at various BaF loading were studied at 150°C by using Curelaster (VDP Orientec Corporation, Japan). A test specimen of the vulcanisable RFCs is inserted into the curometer test cavity and closed under positive pressure 343 kPa. The cavity is maintained at 150°C. The disk is oscillated 100 cycles per minute. The force required to oscillate the disk to the maximum amplitude is continuously recorded as a function of time, and the time required to cure the test specimen is a function of cure characteristics of the rubber compound. Thus, from the cure curve obtained, the cure parameters such as ML, maximum torque (MH), and cure time are evaluated.

The specimens for dynamic measurements were prepared by molding RFCs into thin sheets with 2-mm thickness at 150°C under 140 kg/cm<sup>2</sup> hydraulic pressure. The vulcanization was carried out up to the respective cure times of the samples. The variation of storage modulus  $E'$ , loss modulus  $E''$ , and damping factors  $\tan\delta$  of RFCs with temperature was



**Figure 1** SEM image for the coprecipitated barium ferrite powder.

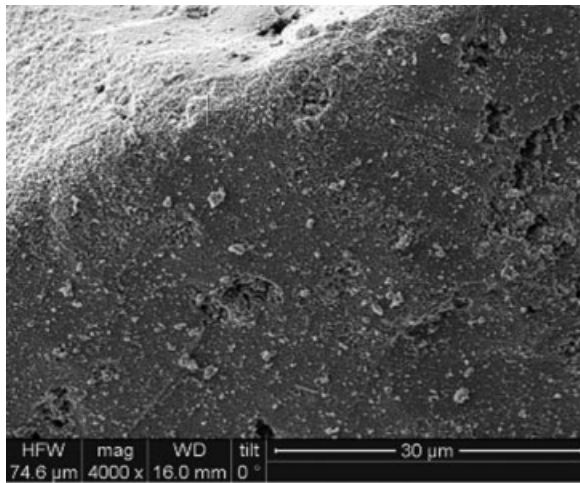
measured by means of a forced vibration viscoelastometer (DVE-V4, Rheology Co., Japan). The measuring frequency was 5 Hz, the strain amplitude was 5  $\mu\text{m}$ , and the heating rate was 3°C/min. Scanning electron microscope (SEM) observations were performed for the RFCs. The SEM samples were prepared by fracturing the samples and polishing the surfaces under liquid nitrogen, followed by carbon coating.

## RESULTS AND DISCUSSION

### Dispersion of BaF in NR matrix

The microstructure for the barium ferrite powder (BaF) is shown in Figure 1. It is clear that the particles have irregular shapes and lie in the range of 45–200  $\mu\text{m}$ . One of the unusual characteristics discovered of the coprecipitated hexagonal barium ferrite  $\text{BaFe}_{12}\text{O}_{19}$  particles is the high porosity with rough surfaces as shown in Figure 2. To our knowledge, such a phenomenon is first observed, and it causes an excellent adhesion between these types of particles and the rubber matrix. These excellent powder natures can be ascribed to the coprecipitation method. Hence, the particles can be stress free because no milling processes are exerted to the powder. This is one of the reasons why the high coercivity of the ferrite particles was obtained in our previous research, even though the particles is multidomain.<sup>17</sup>

Figure 3(a–d) show the distribution of ferrite particles in rubber matrices. The variation of particle sizes, the broad particle distribution, and the homogeneous dispersion can be observed. It also noticed there is no tendency to form agglomerates in the present RFCs even at high loading level. From



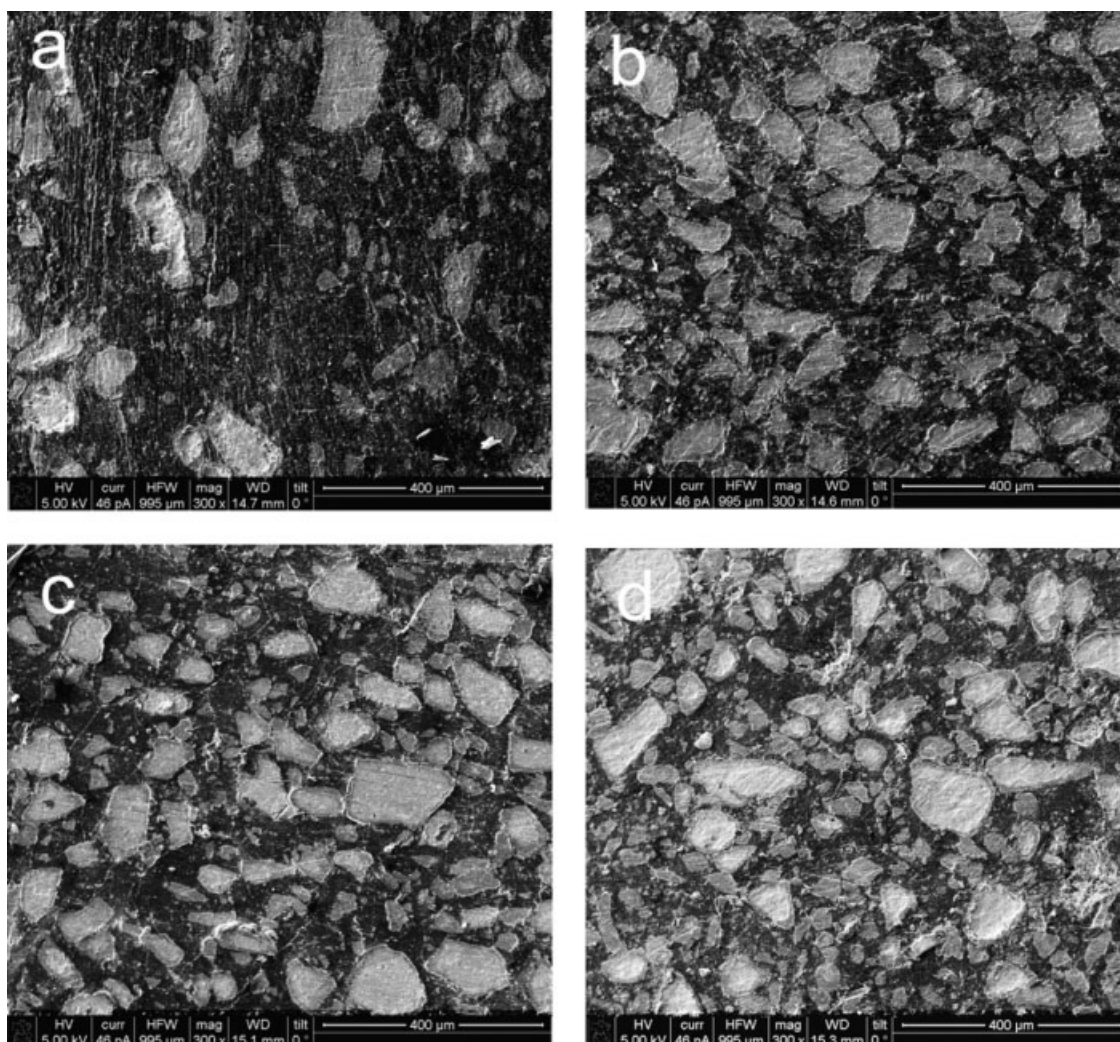
**Figure 2** Detailed surface SEM image for the barium ferrite particles.

Figure 2(b,c), where the ferrite loading was 160 and 180 phr, respectively, we can observe the initial formation of a cohesive network for the ferrite particles

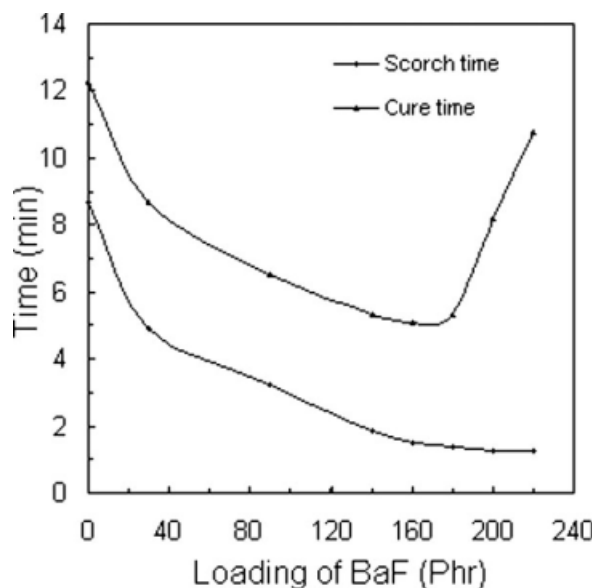
in the rubber matrix, leading to percolation above 180 phr, which is very high in comparison with any different types of fillers.<sup>18–24</sup> The retarding of percolation to very high loading level, is also unexpected behaviors for the present composites, and it can be attributed to the nature of ferrite particles and the degree of mixing, which are critical factors in controlling the physical properties of a polymer-bonded magnet.<sup>25</sup>

### Cure characteristics

The variation of scorch time ( $t_{10}$ ) and cure time ( $t_{90}$ ) as a function of ferrite loading are indicated in Figure 4. The results show that the scorch time decreases dramatically with increasing ferrite content until 160 phr BaF loading, because the heat of mixing increases as the filler loading increases. Further addition of ferrite does not make any appreciable change in scorch time. The saturation of scorch time after that is attributed to the starting formation



**Figure 3** SEM images for the RFCs samples with different ferrite loading: (a) 90 phr, (b) 160 phr, (c) 180 phr, and (d) 220 phr.



**Figure 4** Variation of scorch time and cure time versus ferrite loading.

of a filler network inside the rubber matrix. Consequently, the heat of mixing becomes sufficient, saturated, and independent of ferrite loading, leading to no change in  $t_{10}$ . On the other hand, cure time, which is the total time required for optimum vulcanization of the samples, decreases sharply with increasing ferrite loading at low ferrite content because of the decreasing of scorch time. This result can also be related to the fact that  $\text{BaFe}_{12}\text{O}_{19}$  particles are isotropic in nature, have a small nucleation effect, and interact strongly with rubber.<sup>26</sup> Furthermore, the reduction of cure time of the filled vulcanizates can be attributed to the higher time the rubber compound remain on the mill during mixing. As the filler loading increases, the time of incorporation also increases consequently, generating more heat due to the fraction.

After 160 phr BaF loading, the cure time starts to increase sharply with increasing ferrite content, in contrast with the saturation in scorch time as evidence of deceleration of the vulcanization process after a critical ferrite loading. Earlier studies have indicated that longer cure time is due to better interaction between filler and matrix.<sup>27,28</sup> Therefore, it can be predicted that the increase of the contact surfaces between ferrite particles and rubber matrix at high ferrite loading, in addition to the porous surface of BaF particles, will enhance the adhesion between the present ferrite particles and NR matrix.

From another point of view, the delaying of cure time for polymer composites with increased filler content is always accompanied by adsorption of the accelerators or sulfurs from the filler particle surface, which leads to cure retardation.<sup>29–31</sup> Therefore, one

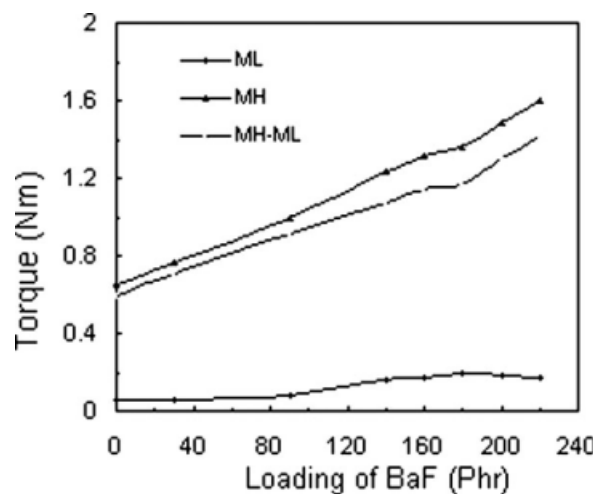
can expected that the increasing of cure time after 160 phr in the current case may be related to these phenomena, especially when the effect of particles surface becomes predominant at high loading. However, the detailed behavior of this phenomena is still uncertain in such high-level loading of barium ferrite in NR. Hence, future works are required to study the nature of the surface interaction between rubber matrixes and barium ferrite particles.

The effect of ferrite loading on the ML and MH is illustrated in Figure 5. ML, which is directly related to the viscosity of the compound at the test temperature, increases with increasing ferrite loading up to percolation limit. After 180 phr BaF loading, ML reached the saturation value due to dilution effects, as a result of the diminishing volume fraction of the polymer in the composites.<sup>32</sup> MH, which is an indication of the modulus of the vulcanized composites, increases with increasing ferrite loading.

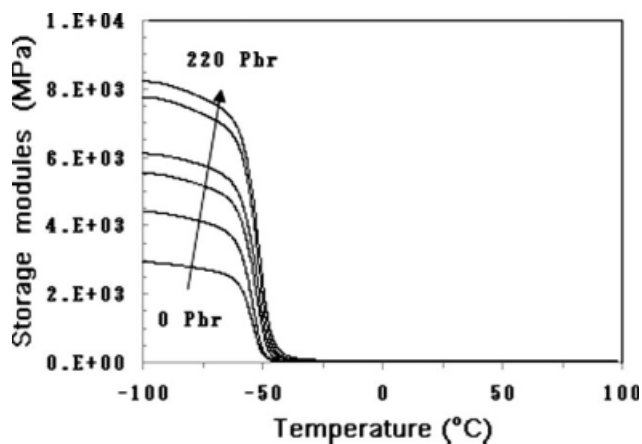
The difference between MH and ML could be used as an indirect indication of the crosslink density of the rubber vulcanizates.<sup>33</sup> As seen in Figure 4, the torque difference, and thus, the crosslink density increase continuously with increasing ferrite loading. This crucial results explain and support the increasing of cure time after percolation and at the same time confirm that the present barium ferrite enhance the curing properties of the composites.

### Dynamic properties

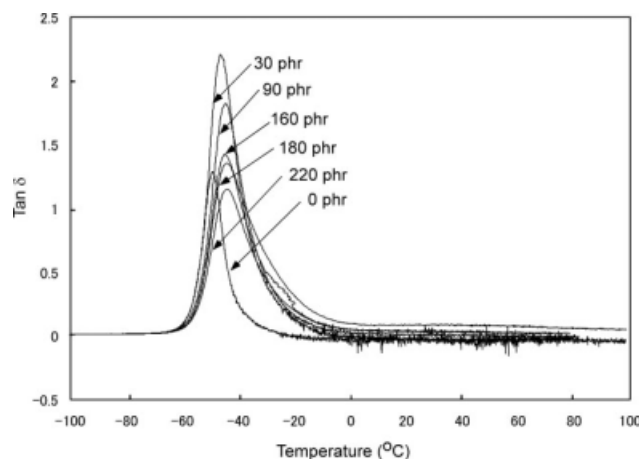
The variation of  $\epsilon'$  and  $\epsilon''$  with temperature at different ferrite loading is shown in Figures 6 and 7, respectively.  $\epsilon'$  found to be increasing with increasing ferrite loading, recording maximum values at low temperature (2930–8213 MPa) for 0 and 180 Phr,



**Figure 5** Variation minimum torque, maximum torque, and torque's difference versus ferrite loading.



**Figure 6** Variation of storage modulus with temperature at different ferrite loadings.



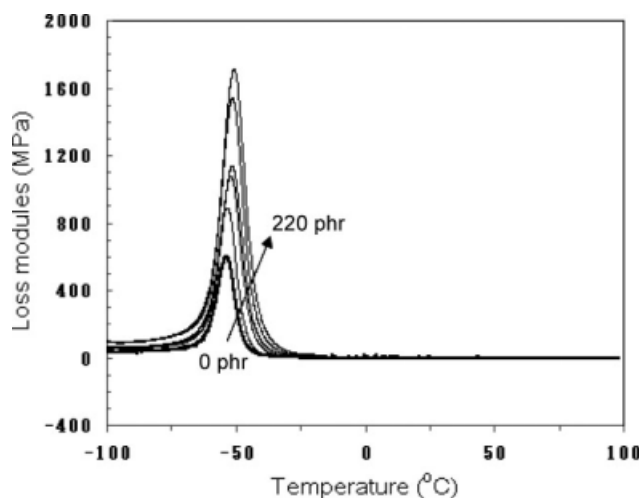
**Figure 8** Variation of loss factor with temperature at different ferrite loadings.

respectively. By increasing the temperature,  $\varepsilon'$  decreases for all samples where steep decreasing was observed when the glass transition temperature of the composites is approached and corresponding maximum in  $\varepsilon''$  is found.

A small change in glass transition temperature ( $t_g$ ) was recorded by increasing the ferrite loading Figure 8. Pure rubber shows  $t_g = -48.5^\circ\text{C}$  and for all ferrite loading  $t_g = -45^\circ\text{C}$ . This small shift to higher temperatures could be associated with the imposed restriction due to the interaction between the filler and rubber matrix.<sup>34</sup> The higher values of tan delta ( $\tan\delta$ ) at  $t_g$  are greater than those of the pure rubber. This is not intuitively expected, because  $\tan\delta$  should ideally decrease with increasing ceramic content. However, this may be ascribed to the perfect bonding between rubber matrix and particles.<sup>35</sup> In addition,

even at high filler loading, the damping characteristics are not significantly affected. This is interesting, as it correlates well with the cure characteristics of the composites. In other words, the present composites have linear viscoelastic behavior as a result of homogeneity and compatibility.<sup>36</sup>

Generally, cure enhancement can be attributed to the filler-related parameters, such as surface area, surface reactivity, particle size, moisture content, and metal oxide content.<sup>8,27</sup> BaF is one of the typical metal oxides that usually achieve excellent adhesiveness with rubber. In addition, the present filler particles had a low surface area activity because of uniform desegregation inside the rubber matrix and its special surface nature as mentioned before. These may be the reasons for delaying cure retardation of the composite to very high ferrite level.



**Figure 7** Variation of loss modulus with temperature at different ferrite loadings.

## CONCLUSION

The coprecipitated ferrite particles play an important role in controlling the processing and dynamic properties of RFCs due to the nature of their surfaces. Sudden change in cure time nevertheless saturation in scorch time around percolation was attributed to the better interaction between filler and rubber matrix. Even at high filler loading, the damping characteristics are not significantly affected. Correlations between cure characteristics and dynamic properties for the present composite were clearly seen. The increase in  $\tan\delta$  with increasing ferrite content indicates perfect bonding between the matrix and particles.

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## References

1. Smit, J.; Wijn, H. P. J. Ferrites; Philips Technical library: Tokyo, 1959–1965.
2. Milke, E. C.; Rei, M.; de Souza, J. P.; Schaeffer, L. *Int J Powder Metall* 2001, 37, 47.
3. Otaigbe, J. U.; Kim, H. S.; Xiao, J. *Polym Compos* 1999, 20, 697.
4. Wang, M.-J. *Rubb Chem Tech* 1998, 72, 430.
5. Fiske, T. J.; Gokturk, H. S.; Kalyon, D. M. *J Mater Sci* 1997, 32, 5551.
6. Puryanti, D.; Hj Ahmad, S.; Hj Abdullah, M. *Polym Plast Tech Eng* 2006, 45, 561.
7. George, W. *Hand book of Filler*; William Andrew Publisher: New York, 1999.
8. Malini, K. A.; Mohammed, E. M.; Sindhu, S.; Joy, P. A.; Date, K.; Kulkarni, S. D.; Kurian, P.; Anantharaman, M. R. *J Mater Sci* 2001, 36, 5551.
9. Vinod, V. S.; Varghese, S.; Kuriakose, B. *J Adhes Sci Technol* 2000, 14, 1105.
10. Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymer and Composites*; Marcel Dekker Inc: New York, 1974.
11. Sirisinha, C.; Phoowakeereewiwat, S.; Saeoui, P. *Eur Polym J* 2004, 40, 1779.
12. Solomon, M. A.; Kurian, P.; Joy, P. A.; Anantharaman, M. R. *Int J Polym Mater* 2004, 53, 565.
13. Solomon, M. A.; Kurian, P.; Anantharaman, M. R.; Joy, P. A. *Polym Plast Tech Eng* 2004, 43, 1028.
14. Saini, D. R.; Nadkarni, V. M.; Grover, P. D.; Nigam, K. D. P. *J Mater Sci* 1986, 21, 3710.
15. Solomon, M. A.; Kurian, P.; Anantharaman, M. R.; Joy, P. A. *J Elast Plast* 2005, 37, 109.
16. Makled, M. H.; Matsui, T.; Tsuda, H.; Mabuchi, H.; El-Mansy, M. K.; Morii, K. *J Mater Process Technol* 2005, 160, 229.
17. Makled, M. H.; Matsui, T.; Tsuda, H.; Mabuchi, H.; El-Mansy, M. K.; Morii, K. *J Ceram Soc Jpn* 2004, 112, 200.
18. Razzaq, M. Y.; Anhalt, M.; Frommann, L.; Weidenfeller, B. *Mater Sci Eng* 2007, 444, 227.
19. Barra, G. M. O.; Jacques, L. B.; Orefice, R. L.; Carneiro, J. R. G. *Eur Polym J* 2004, 40, 2017.
20. Stejskal, J.; Trchova, M.; Brodinova, J.; Kalenda, P.; Fedorova, S. V.; Prokes, J.; Zemek, J. *J Colloid Interface Sci* 2006, 298, 87.
21. Ke, W.; Zhang, N.; Geng, T.; Gao, R. *J Mag Magn Mater* 2007, 312, 430.
22. Reich, S. *J Mater Sci* 1987, 22, 3391.
23. Li, Y.-J.; Xu, M.; Feng, J.-Q.; Dang, Z.-M. *Appl Phys Lett* 2006, 89, 072902.
24. Murphy, R.; Nicolosi, V.; Hernandez, Y.; McCarthy, D.; Rickard, D.; Vrbancic, D.; Mrzel, A.; Mihailovic, D.; Blau, W. J.; Coleman, J. N. *Scripta Mater* 2006, 54, 417.
25. Xiao, J.; Otaigbe, J. U. *J Mater Res* 1999, 14, 2893.
26. Sobahy, M. S.; El-Nshar, D. E.; Maziad, N. A. *Egypt J Sol* 2003, 26, 241.
27. Jacob, M.; Thomas, S.; Varughese, K. T. *Compos Sci Technol* 2004, 64, 955.
28. Ismail, H.; Rusli, A.; Rashid, A. A. *Polym Test* 2005, 24, 856.
29. Ismail, H.; Abdul Khalil, H. P. S. *Polym Test* 2001, 20, 33.
30. Nakason, C.; Kaesaman, A.; Eardrod, K. *Mater Lett* 2005, 59, 4020.
31. Shanmugaraj, A. M.; Bae, J. H.; Yong Lee, K.; Noh, W. H.; Lee, S. E. H.; Ryu, S. H. *Compos Sci Tech* 2007, 67, 1813.
32. Anantharaman, M. R.; Jagatheesan, S.; Sindhu, S.; Malini, K. A.; Chinnasamy, C. N.; Narayanasamy, A.; Kurian, P.; Vasudevan, K. *Plast Rubb Compos Process* 1998, 27, 77.
33. Sae-Oui, P.; Sirisinha, C.; Thepsuwan, U.; Hatthapanit, K. *Eur Polym J* 2007, 43, 185.
34. Falco, A. D.; Goyanes, S.; Rubiolo, G. H.; Mondragon, I.; Marzocca, A. *Appl Surf Sci* 2007, 254, 262.
35. Marra, S. P.; Ramesh, K. T.; Douglas, A. S. *Comp Sci Technol* 1999, 59, 2163.
36. Lipatov, Y. S. *Polymer Reinforcement*; Chem Tech Publishing: Toronto, Canada, 1995.