

Nanotechnology in elastomers- Myth or reality

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Abstract: Nanotechnology is the fast becoming key technology of the 21st century. Due to its fascinating size-dependent properties, it has gained significant important in various sectors. Myths are being formed on the proverbial nanotechnology market, but the reality is the nanotechnology is not a market but a value chain. The chain comprises of - nanomaterials (nanoparticles) and nanointermediates (coatings, compounds, smart fabrics). Elastomer based nanocomposites reinforced with low volume fraction of nanofillers is the first generation nanotechnology products and it has attracted great interest due to their fascinating properties. The incorporation of nanofillers such as nanolayered silicates, carbon nanotubes, nanofibers, metal oxides or silica nanoparticles into elastomers improves significantly their mechanical, thermal, barrier properties, flame retardancy etc., Extremely small particle size, high aspect ratio and large interface area yield an excellent improvement of the properties in a wide variety of the materials. Uniform dispersion of the nanofillers is a general prerequisite for achieving desired properties. In this paper, current developments in the area of elastomer based nanocomposites reinforced with layered silicate and carbon nanotube fillers are highlighted.

1. Introduction

Nanotechnology is a highly interdisciplinary field, in which researchers strive to control matter on the nanoscale. Nanotechnology is defined as the engineering of functional systems at scales of less than 100 nanometers (nm) to achieve size-dependent properties and functions. Nowadays, polymer based nanocomposite materials are applied in almost all areas of our life and they have stimulating function

for the development of future technologies. In contrast to metallic and ceramic particles, polymers are relatively cheap, can be easily processed into a desired shaping, and have wide variety application aspects in textiles, electromagnetic shielding, coatings, automotive parts, electronic and household appliances etc. Polymer nanocomposites incorporated with nanostructured materials are termed as first gen-



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eration products of nanotechnology and they are interpreted as passive nanostructures. These composites are multiphase solid materials, where one of the phases has stiff, inorganic and anisotropic nanostructures (size <100 nm). Incorporation of the nano-sized fillers such as nanoclay, metal nanoparticles or carbon nanotubes in polymer results in the high performance composite materials that satisfy the basic property needs such as excellent flammability, thermal stability, mechanical and barrier properties.¹

Nanocomposite materials prepared using nanofillers and elastomers are termed as elastomeric nanocomposites, which can also be interpreted as passive nanostructures or first generation products of nanotechnology. Elastomers are a very important class of polymeric materials and the generation of their nanocomposites by the incorporation of nanofillers has led to significant enhancement of their properties and thereby expansion of their application potential. Significant improvement in the properties on loading fillers in the elastomers is often termed as reinforcement in the elastomer sectors. This reinforcement behavior in elastomers is observed at very low loading of nanofillers, typically less than 10 wt% compared to the conventional fillers such as carbon black or silica (30-70 wt%). Because of their high aspect ratio (length/diameter) and low density, nanofillers can be used to substitute to traditional fillers in the elastomeric nanocomposites. Nanostructured fillers such as layered silicates, ceramic nanoparticles, (such as silica, titania, zirconia etc.), carbon nanofibers, and nanotubes are the typical examples of materials used as nano-reinforcing additives in the elastomeric nanocomposites. The major application aspects of elastomeric nanocomposites are electromagnetic interference shielding (EMI) applications, tire applications and nanocomposite barrier coatings. The major advantage of replacing conventional fillers with nanofillers in

elastomeric composites is the fabrication of light weight composites suitable of various applications. Also, better load transfer and increase in crack propagation length are the merits of replacing the conventional fillers by nanofillers in the elastomeric nanocomposites. However, the major challenges associated with nanofiller reinforced elastomeric composites are nanofiller aggregation in elastomers during the manufacturing process that hampers the property improvement and the environmental threats of handling nanosized fillers in the industrial environment. This article reviews the industrially viable facile preparation process of elastomeric nanocomposites by referring suitable research articles.

2. Elastomer/layered silicate nanocomposites

The most common reinforcement nanofiller used in elastomers are clay minerals consisting of layered silicate structures. It consists of regularly stacking of layered silicate platelets with approximate thickness of 1 nm held together by weak dipolar forces leading to interlayer's or galleries between the layers. A representative layered silicate material (Montmorillonite clay) is shown in Figure 1. The intergallery layers of these clay minerals are generally occupied

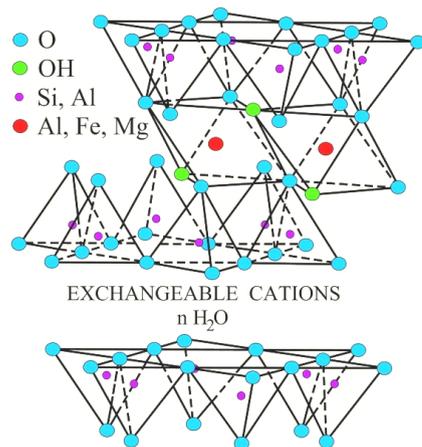


Figure 1. Structure of Montmorillonite clay.

by cations such as Na^+ , Mg^{2+} or Ca^{2+} , which are usually replaced by organic cations such as alkyl ammonium cations via ion exchange reaction resulting in organophilic clay. These organophilic clays are more compatible with polymers leading to the high performance polymer nanocomposites.

Elastomer/layered silicate nanocomposites is the hybrid material consisting of layered silicates dispersed in the elastomer matrix in the form of reticular layer of crystals about 1 nm thickness and with the lamellar aspect ratio of 100 to 1000. Significant research has been done on the preparation of elastomer/clay nanocomposites using various elastomers.²⁻⁴ Incorporation of nanoclay platelets on elastomers improves the mechanical properties,⁵ fracture toughness,⁶ flame retardancy,⁷ barrier,⁸ thermal⁹ and oil resistant properties.¹⁰ The essence of this property improvement is due to the nanoscale dispersion¹¹ of clay as well as its high aspect ratio.¹² Basically three different dispersion states of clay in elastomer matrix is observed as depicted in Figure 2. The first type of dispersion state is a non-exfoliated system where nanoclay particles are seen to remain as stacked structure consisting of a very large number of platelets with interlayer spacing equivalent to that of neat clay (unmixed state as depicted in Figure 2). The second type of dispersion state is an intercalated case, wherein an expansion of clay platelets is observed resultant of polymer chain penetration into the interlayer spacing, which is depicted as intercalated state in Figure 2. The third type of dispersion state of elastomeric nanocomposite is the exfoliated state, where the individual nanosilicate layers are finely distributed in the elastomer matrix. Engineering performance of elastomeric nanocomposites is maximum only if the dispersion states of clay in the elastomer should be the co-existence of intercalated-exfoliated structure.

The most common methods for the preparation of

elastomer-clay nanocomposites are solution blending, melt blending, in-situ polymerization and latex compounding. Among these techniques, the industrially viable technique is melt blending as this method is environmentally benign due to the absence of organic solvents and it is compatible with current industrial processes such as extrusion and injection molding. Significant research has been done by various research groups on the melt blending techniques in developing elastomeric nanocomposite.¹³⁻¹⁵ Though it is expected that acting shear forces strongly favour the exfoliation of layered silicates during melt compounding, the overall dispersion states of the clay in the elastomer matrix is poor that results in the decrement of properties. The most industrially viable technique in preparing elastomer nanocomposites is the latex compounding method through which the clay layers can be exfoliated and homogeneously dispersed in the polymer matrix at the nano level.

The preparation of elastomer/clay nanocomposites through latex compounding technique can be done by two different processes viz. (i) Latex co-coagulating technique (ii) Latex blending technique.

In latex co-coagulating technique, the clay plate-

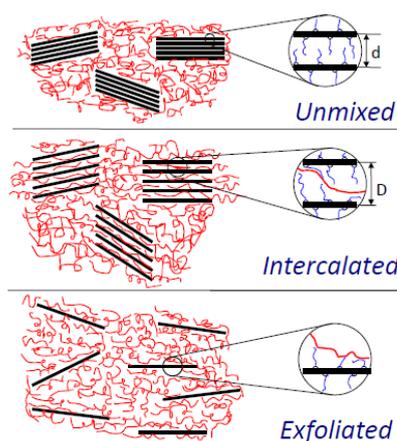


Figure 2. Schematic representation on the dispersion states of clay filled elastomers.

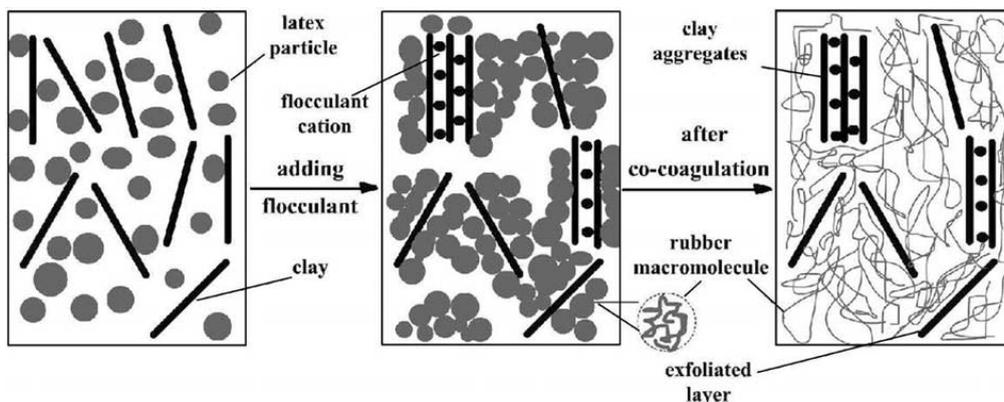


Figure 3. Schematic representation of elastomer/ clay nanocomposites prepared through latex co-coagulating technique.

lets are initially dispersed in the elastomer latex followed by the addition of flocculent that result in the aggregation of latex particles consisting of elastomer macromolecules. Addition of co-coagulating agent results in the coalescence of the aggregated latex particles leading to the formation of elastomer/clay masterbatch as depicted in Figure 3. These masterbatches are further processed through conventional melt blending techniques with the addition the compounding ingredients leading to the formation of elastomer/clay nanocomposites. The mechanical and barrier properties of the elastomer nanocomposites prepared through latex co-coagulating method are significantly higher compared to the melt blending techniques.¹⁶ Latex blending technique is quite similar to latex co-coagulating technique with the slight variation in process conditions. In latex blending technique, compounding ingredients are added along-with the clay dispersant prior to co-coagulation of the latex resulting in the formation of elastomer/clay nanocomposites. Mitra et al.,¹⁷ reported that elastomer/clay nanocomposite prepared through latex blending technique results in complete exfoliation of clay in the elastomer matrix compared to latex co-coagulating technique (Figure 4).

Elastomer/layered silicate nanocomposites has

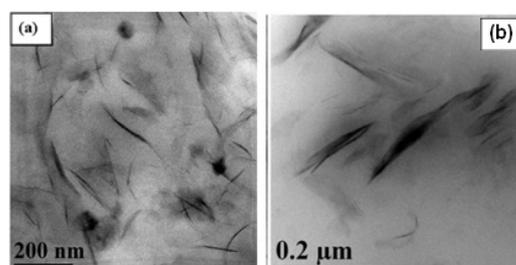


Figure 4. TEM images of SBR/clay nanocomposites prepared through latex blending (a) and latex co-coagulating (b) techniques.

achieved commercial importance in the area of nanocomposite coatings due to the excellent improvement on the barrier properties of the elastomer on nanoclay loading. For instance, butyl rubber/layered silicate nanocomposites based coatings shows excellent improvement in the barrier properties and hence they are generally used as elastomeric barrier coatings for sports ball, tires, chemical protection gloves etc.

3. Elastomer/carbon nanotube composites

Carbon nanotubes can be visualized as graphene layers rolled into cylinders consisting of a planar hexagonal arrangement of carbon-carbon bonds. Their outstanding properties are a consequence of this unique bonding arrangement combined with

topological defects required for rolling up the sheets of graphite into cylinders. During growth, depending on the synthesis methods, they can assemble either as concentric tubes (multiwall nanotubes, MWNTs) or as individual cylinders (single-wall nanotubes, SWNTs). Their diameters range from about a nanometer to tens of nanometers with lengths ranging from several micrometers to millimeters or even centimeters.

Composites obtained by dispersing nanotubes into different elastomers have attracted wide attention in order to develop ultra-lightweight and extremely strong materials. In elastomer composites, filler dispersion as well as interfacial interactions has been shown to be crucial parameters for enhanced mechanical properties. The major factor affecting the homogeneous dispersion of carbon nanotubes in a polymer matrix is the van der Waals interactions between individual tubes that leads to significant aggregation or agglomeration, thus reducing the expected property improvements of the resulting com-

posite. But to date, despite the fact that much progress has been made in the processing techniques, the mechanical improvement brought about by incorporation of nanotubes remains minor with regard to the potential based on the properties of the nanotube itself.

The techniques, which are normally used to prepare elastomeric/nanotube composites are solution mixing, melt compounding and in situ miniemulsion polymerization. Significant research has been done on the preparation of elastomeric nanocomposites through various processing methods.¹⁴ Of all these techniques, the industrially viable technique is the melt compounding in which shear forces are used to separate the individual nanotubes in the elastomer matrix to get a homogeneous dispersion throughout the matrix. However, re-agglomeration of carbon nanotube in the elastomer matrix is the major drawback that limits its real potential. To overcome this issue, chemically functionalized carbon nanotubes that impart adhesion between the nanotube and elas-

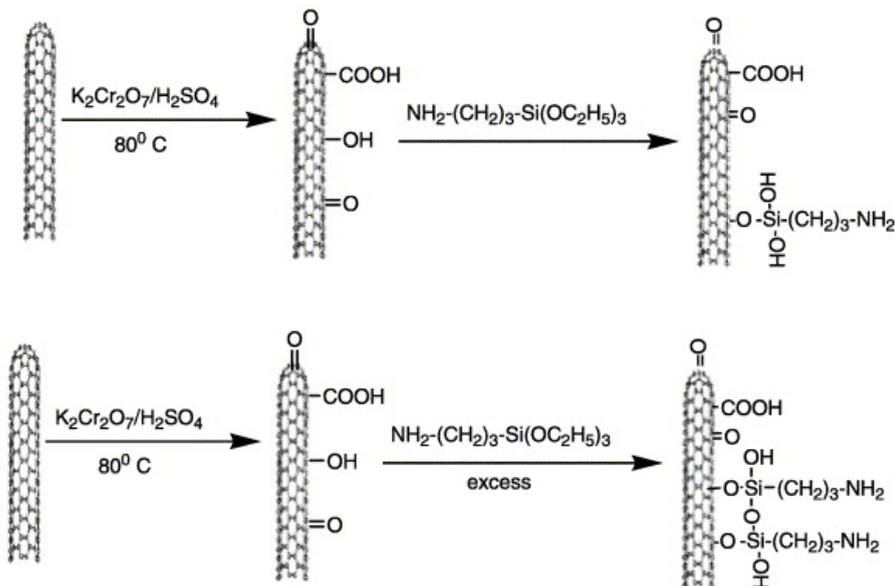


Figure 5. Schematic representation of carbon nanotube functionalization.

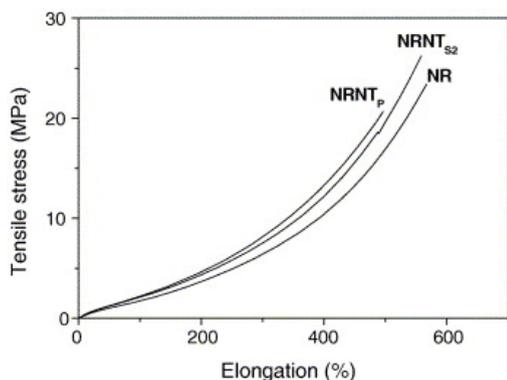


Figure 6. Stress-strain graph natural rubber (NR), natural rubber/pristine carbon nanotube (NRNT_P) and natural rubber/silane functionalized carbon nanotube composites (NRNT_{S2}).

elastomer chains are often used to prepare elastomeric nanocomposites as it enables effective stress transfer at the polymer-filler interface. The role of functionalized carbon nanotubes on the properties of the various elastomers are investigated by various researchers.

Shanmugaraj et al.,¹⁸ functionalized the carbon nanotube by grafting aminopropyl triethoxysilane (Figure 5) and they observed improvement in mechanical properties on loading these modified carbon in natural rubber matrix (Figure 6). A recent report revealed that loading of anisotropic carbon nanotubes in thermoplastic elastomers such as polyurethane results in the rise of rubbery modulus and thereby shape fixity by enhancing strain induced crystallization, which demonstrates its technological uses ranging from shape-recovery eye-glass frames to temperature sensitive switches.¹⁹

Elastomer/carbon nanotube composite has achieved commercial importance in the area of conductive nanocomposite coatings, blow-out protectors and electromagnetic interference shielding (EMI) applications due to the excellent improvement on the electrical properties and oil resistance property of the

elastomer on carbon nanotube loading. For instance, carbon nanotube filled nitrile rubber composites are used for the fabrication of blow-out protectors with excellent oil-resistant properties.

4. Conclusions

Since nanotechnology has gained significant importance in recent years, their application aspects in various sectors has been explored. Nanotechnology in elastomers is the first generation nanotechnology products, which comprises of nanofiller finely dispersed in the elastomer matrix with significant improvement in the mechanical, barrier, electrical and flame retardency properties. Due to its unique fascinating properties, they find applications as nanocomposite coating materials, blow-out protectors and EMI shielding materials.

References

1. H. Koerner, G. Price, N. A. Pearce, M. Alexander, and R. A. Vaia, *Nature Mater.* **3**, 115 (2004).
2. Y. W. Chang, Y. Yang, S. Ryu, and C. Nah, *Polym. Int.*, **51**, 319 (2002).
3. C. Nah, H. J. Ryu, S. H. Han, J. M. Rhee, and M. H. Lee, *Polym. Int.*, **50**, 1265 (2001).
4. H. Ismail and R. Ramli, *J. Reinforce. Plastics. Compos.*, **27**, 1909 (2007).
5. C. A. Rezende, F. C. Braganca, T. R. Doi, L. -T. Lee, F. Galembeck, and F. Boue, *Polymer*, **51**, 3644 (2010).
6. M. Alexandre and P. Dubois, *Mater. Sci. Engg: R: Reports*, **28**, 1 (2000).
7. P. Kiliaries and C. D. Papaspyrides, *Prog. Polym. Sci.*, **35**, 902 (2010).
8. Y. Liang, W. Cao, Z. Li, Y. Wang, Y. Wu, and L. Zhang, *Polym. test.*, **27**, 270 (2008).
9. J. Gilman, *Appl. Clay. Sci.*, **15**, 31 (1999).
10. S. Pavlidou and C. D. Papaspyrides, *Prog. Polym. Sci.*, **33**, 1119 (2008).
11. L. Liu, D. M. Jia, Y. F. Luo, and B. C. Guo, *J. Appl. Polym. Sci.*, **100**, 1905 (2006).
12. Y. Z. Wang, L. Q. Zhang, C. H. Tang, and D.

- S. Yu, *J. Appl. Polym. Sci.*, **78**, 1879 (2000).
13. Z. Susteric and T. Kos, *Macromol. Sympos.*, **296**, 311 (2010).
14. R. Sengupta, S. Chakraborty, S. Bandyopadhyay, S. Dasgupta, R. Mukhopadhyay, K. Andy, and A. S. Deuri, *Polym. Engg. Sci.*, **47**, 1956 (2007).
15. D. Huang, Y. R. Tang, T. C. Zhang, and S. Z. Zhan, *J Appl. Polym. Sci.*, **117**, 2870 (2010).
16. Y. -P. Wu, Y. -Q. Wang, H. -F. Zhang, Y. -Z. Wang, D. -S. Yu, L. -Q. Zhang, and J. Yang, *Compos. Sci. Technol.*, **65**, 1195 (2005).
17. S. Mitra, S. Chattopadhyay, and A. K. Bhowmick, **118**, 81 (2005).
18. A. M. Shanmugharaj, J. H. Bae, K. Y. Lee, W. H. Noh, S. H. Lee, and S. H. Ryu, *Compos. Sci. Technol.*, **67**, 1813 (2007).
19. H. Koerner, G. Price, N. A. Pearce, M. Alexander, and R. A. Vaia, *Nat. Mater.*, **3**, 115 (2004).