



Investigation of Exfoliation and Intercalation in Clay Nanocomposites

Daver Ali

Department of Mechanical Engineering, Ataturk University, Turkey

Corresponding author E-mail: daali935@gmail.com

Short Communication

Received 4 Oct. 2011

Accepted 17 Nov. 2011

Published 30 Dec. 2011

Keywords:

Exfoliation & Intercalation
Clay
Nanocomposites

Abstract

In this study the effect of filling of clay nanoparticle in the polymer base composite and the intercalation, exfoliation of these nano particle has been reviewed. Furthermore the process of these phenomena has been looked back. The intercalation is a state that is introduction of exfoliation. It is concluded that completed exfoliation of silicate layers is the fundamental to reaching polymer/clay nanocomposites that perform well.

INTRODUCTION

Nanocomposites are a relatively new type of composite materials with ultra-fine phase dimension typically in the range of 1–100 nm[1]. Because of their unique phase morphology and their improved interfacial properties, these materials usually exhibit better physical and mechanical performance than the micro one. In general, there are two kinds of nanocomposites, namely intercalated and exfoliated [2].

Research and development of nanocomposites consisting of exfoliated smectite clays in cross-linked polymers have been growing [3] Much attention has been concentrated on the realization and control of the exfoliation of clay layers [4]. But the exfoliation behavior and mechanism are still not very clear. Intercalation polymerization was first success fully used in manufacturing nylon6/montmorillonite nanocomposites, which show greatly improved thermal, mechanical, barrier, and even flame-retardant properties compared with their conventional inorganic particle-filled counterparts[5]. Many works have proved that a completed exfoliation of silicate layers is the key to achieving polymer/clay nanocomposites that perform well[6]. found that the exfoliation behavior of clays was determined mainly by the structure of the organoclays and the curing temperature adopted[7]. The organoclays can be easily intercalated by epoxy polymer through a mild mixing at 70 – 80 °C to form a homogenous and stable organoclay/epoxy intercalated hybrid[8]. In general, the

dispersion of clay particles in the resin matrix can result in the formation of three general types of composite[7]:

(a) Normal composites

(b) Intercalated nanocomposites: it is formed by the insertion of polymer molecules in to the clay host galleries and the clay remains a regular gallery structure, although the basal spacing rises

(c) Exfoliated nanocomposite

Both intercalated and exfoliated nanocomposites offered some special physical and mechanical properties compared to the normal composites, and some nano composites such as nylon 6/clay[9], PA/clay[10], PS/clay[11], PMMA/clay[12], PP/clay[13], polyimide/clay [14]and PU/clay[15]have been produced in the lab and in industry in recent years.

Intercalation-Exfoliation

Layered silicate can be induced to exfoliate in to nano-scale layers, which disperse in the polymer matrices uniformly. This process is called intercalation polymerization. By intercalation and in-situ polymerization of monomers the structure of nanocomposites will form.

If the original sandwich structure of the clay is still retained but the interlayer spacing is increased, the composite formed is called intercalated nanocomposite. If the silicatelayers exfoliate completely and disperse individually in the polymer matrix, an exfoliated nano composite is formed. Generally, exfoliated



nanocomposites exhibit better properties than intercalated nanocomposites. It is known that exfoliation can lead to a better reinforcement effect owing to the

increase in the high aspect ratio of clay layers, and better barrier properties owing to a longer path of molecule penetration [16].

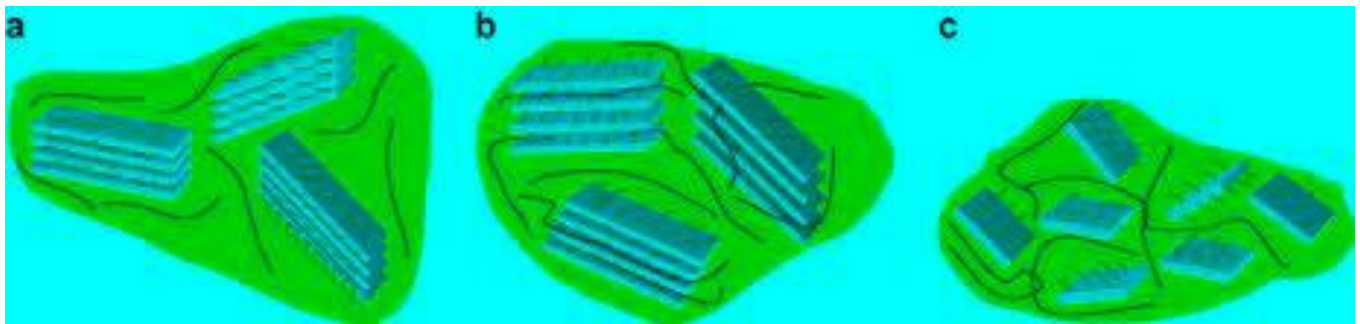


Fig. 2. Morphologies of clay/polymer composites: (a) microcomposite, (b) intercalated, (c) exfoliated.

Methods of Intercalation and Exfoliation

Recently much attention has been paid to developing layered silicate as a reinforcement material for polymers. The preparation method is called intercalation compounding, including intercalative polymerization, solution intercalation, and melt intercalation, among other processes. [17]. In situ polymerization is one of the methods to prepare exfoliated and intercalated polymer/clay nanocomposites. Generally, in situ polymerization includes two stages[2]:

- 1- Mix the polymer precursor or monomer and clay;
- 2- In situ polymerization in the presence of clay.

It is suggested that the in situ polymerization is responsible for the exfoliation of clay layers in the polymer matrix. Exfoliation of clay layers is attributed to the formation of cross linked structures inside the clay galleries during the curing process.

Transmission electron microscopy (TEM) and wide angle X-ray diffraction (XRD) are important methods for characterizing the intercalated and exfoliated structure of clay layers [18]. Nevertheless, both methods can only be employed after the formation of materials and are costly. It is always desirable to have a rapid estimation before the formation of materials. Rheology has attracted a lot of interest [19]. That has been suggested in situ curing of epoxy monomer and hardener leads to the exfoliation of clay layers [20]. The intercalation and exfoliation of talc have been realized by solid state shear compounding using pan mill equipment that can exert fairly strong shear forces and has multi functions such as pulverizing, mixing, and activation on materials[21].

Recently, a novel solid-state approach has been reported to produce polymer/clay nanocomposites. The approach applies pressure to polymer/clay systems, resulting in layer expansion of clay in polymer[22]

CONCLUSION

The intercalation and exfoliation of clay nano particles in polymer matrix have been investigated to approach an improve mechanical, thermal and electrical properties of resulted clay nanocomposites. In situ polymerization is one of the methods that are used for manufacturing of nanocomposites. Furthermore; in situ curing of epoxy monomer and hardener leads to the exfoliation of clay

layers. That is concluded that the quality of intercalation and exfoliation will affect the properties of nano composite strongly.

REFERENCES

1. Giannelis, E.P., *Polymer layered silicate nanocomposites*. Advanced Materials, 1996. **8**(1): p. 29-8.
2. Xia, H.S. and M. Song, *Intercalation and exfoliation behaviour of clay layers in branched polyol and polyurethane/clay nanocomposites*. Polymer International, 2006. **55**(2): p. 229-235.
3. Brown, J.M., D. Curliss, and R.A. Vaia, *Thermoset-layered silicate nanocomposites. quaternary ammonium montmorillonite with primary diamine cured epoxies*. Chemistry of Materials, 2000. **12**(11): p. 3376-3384.
4. Ma, J., et al., *A novel method for preparation of disorderly exfoliated epoxy/clay nanocomposite*. Chemistry of Materials, 2004. **16**(5): p. 757-759.
5. Wang, C.Y., et al., *Weighted semiparametric estimation in regression analysis with missing covariate data*. Journal of the American Statistical Association, 1997. **92**(438): p. 512-525.
6. Shi, H.Z., T. Lan, and T.J. Pinnavaia, *Interfacial effects on the reinforcement properties of polymer-organoclay nanocomposites*. Chemistry of Materials, 1996. **8**(8): p. 1584-8.
7. Lan, T., P.D. Kaviratna, and T.J. Pinnavaia, *Mechanism of Clay Tactoid Exfoliation in Epoxy-Clay Nanocomposites*. Chemistry of Materials, 1995. **7**(11): p. 2144-2150.
8. Lu, J.K., et al., *Study on intercalation and exfoliation behavior of organoclays in epoxy resin*. Journal of Polymer Science Part B-Polymer Physics, 2001. **39**(1): p. 115-120.
9. Kojima, Y., et al., *Mechanical-Properties of Nylon 6-Clay Hybrid*. Journal of Materials Research, 1993. **8**(5): p. 1185-1189.
10. Liu, L.M., Z.N. Qi, and X.G. Zhu, *Studies on nylon 6 clay nanocomposites by melt-intercalation process*. Journal of Applied Polymer Science, 1999. **71**(7): p. 1133-1138.

11. Sikka, M., et al., *Melt intercalation of polystyrene in layered silicates*. Journal of Polymer Science Part B-Polymer Physics, 1996. **34**(8): p. 1443-1449.
12. Lee, D.C. and L.W. Jang, *Preparation and characterization of PMMA-clay hybrid composite by emulsion polymerization*. Journal of Applied Polymer Science, 1996. **61**(7): p. 1117-1122.
13. He, X.J., et al., *Phylogeny of Chinese Allium (Liliaceae) using PCR-RFLP analysis*. Science in China Series C-Life Sciences, 2000. **43**(5): p. 454-463.
14. Tyan, H.L., K.H. Wei, and T.E. Hsieh, *Mechanical properties of clay-polyimide (BTDA-ODA) nanocomposites via ODA-modified organoclay*. Journal of Polymer Science Part B-Polymer Physics, 2000. **38**(22): p. 2873-2878.
15. Chen, T.K., Y.I. Tien, and K.H. Wei, *Synthesis and characterization of novel segmented polyurethane clay nanocomposite via poly(epsilon-caprolactone)/clay*. Journal of Polymer Science Part a-Polymer Chemistry, 1999. **37**(13): p. 2225-2233.
16. Yoonessi, M., et al., *Preparation, characterization, and properties of exfoliated/delaminated organically modified clay/dicyclopentadiene resin nanocomposites*. Macromolecules, 2004. **37**(7): p. 2511-2518.
17. Okamoto, M., *Polymer/layered silicate nano-composites - Structure development and processing operations*. International Polymer Processing, 2006. **21**(5): p. 487-496.
18. Okamoto, K., S.S. Ray, and M. Okamoto, *New poly(butylene succinate)/layered silicate nanocomposites. II. Effect of organically modified layered silicates on structure, properties, melt rheology, and biodegradability*. Journal of Polymer Science Part B-Polymer Physics, 2003. **41**(24): p. 3160-3172.
19. Ren, J.X., A.S. Silva, and R. Krishnamoorti, *Linear viscoelasticity of disordered polystyrene-polyisoprene block copolymer based layered-silicate nanocomposites*. Macromolecules, 2000. **33**(10): p. 3739-3746.
20. Park, J.H. and S.C. Jana, *Mechanism of exfoliation of nanoclay particles in epoxy-clay nanocomposites*. Macromolecules, 2003. **36**(8): p. 2758-2768.
21. Shao, W.G., Q. Wang, and K.S. Li, *Intercalation and exfoliation of talc by solid-state shear compounding ((SC)-C-3) using Pan-Mill equipment*. Polymer Engineering and Science, 2005. **45**(4): p. 451-457.
22. Gao, F., S. Chen, and J.B. Hull, *Layer expansion of layered silicates in solid polymer matrices by compression*. Journal of Materials Science Letters, 2001. **20**(19): p. 1807-1810.