

ROLES OF NANOPARTICLE FILLERS DURING NANOSTRUCTURE SELF-ASSEMBLY IN THE ENHANCEMENT OF NANOCOMPOSITES BARRIER PROPERTIES

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Abstract

During self-assembly, the nanostructure of materials builds itself 'spontaneously' through local non-covalent interactions. This process of organization consistently applies to the higher meso- and macroscopic scales of ordering and thus governing the materials properties. Self-assembly can be rationally designed and is a practical strategy to build a nanostructure. This review discusses the effect of various manners of self-assembly due to various degrees of interactions between nanoparticle fillers and polymer matrix in enhancing nanocomposites properties, especially the barrier properties, and in particular fire retardancy. The assembly of three-dimensional structures of polyurethanes, for instance, is governed by microphase separation due to hydrogen bonding (10-65 kJ mol⁻¹ of strength) within the hard phases of polyurethane foams (~10 nm of size). The microphase separation is influenced by the existence of nanoparticle fillers in the nanocomposites, to the extent that they may become either nucleation sites and catalysts for cell growth and coalescence, physical hindrance to hydrogen bonding and microphase separation, or perhaps somewhere in between. In the case of flexible polyether-urethane/layered-silicate nanocomposite, it was clearly observed that the presence of a molecular scale ingredient brings about an additional rule of assembly to the reacting mixture, resulting in a relatively better organized structure. Therefore, in order to engineer and control fire retardancy and other barrier properties of nanocomposite materials, the nature and mechanism of their self-assembly in the presence of nanoparticle fillers needs to be well understood.

Keywords: barrier properties, fire retardancy, nanocomposites, nanostructure, polyurethanes, self-assembly.

INTRODUCTION

Polymers are probably the most versatile material with many advantages unreplacable by other materials. However, their flammability limits their use because of the probability of fire occurrence and consequences of a fire in a number of applications within electrical and electronic sector, textile, transportation, building, furniture, and many more. The use of fire retardants must strictly follow health, safety, and environmental regulations, which banned the use of some halogenated compounds and discouraged applications of brominated compounds. Inorganic nanofillers has been studied and used as promising solution to polymer fire retardancy, because a dramatic reduction in combustion rate was observed and simultaneously the physical and mechanical properties of the polymer nanocomposites were improved¹.

Nanoparticles being used as fire retardants, such as nanoclays, showed beneficial effects on combustion of nanocomposites, which are linked to catalytic effects of nanofillers under certain condition¹. As burning reaction accelerated, formation of a protective surface layer comprising a thermally stable combination of carbonaceous char and clays is also enhanced¹. Other promising fire retardant nanoparticles include carbon nanotube (CNT), either single wall (SWNT) or multi wall (MWNT), and polyhedral oligomeric silsesquioxane (POSS). Some nanoparticles like TiO₂ were also explored with no significant improvement in flammability properties². More

studies are needed to modify barrier properties of nanocomposites, particularly ignition delay time and flame persistency¹. A deep understanding of chemical interaction between inorganic nanofillers and organic polymers will facilitate the design of polymer nanocomposites with controlled thermally stability and fire behaviour. In turn, fire-safe, environmentally friendly nanocomposite formulation will evolve.

NANOFILLERS AND SELF-ASSEMBLY OF POLYURETHANE NANOCOMPOSITES

1. Self-Assembly

Recent developments in materials researches have found ample phenomena of 'self-assembly', in which the nanostructure of materials builds itself 'spontaneously' through local non-covalent interactions³. This reversible process of organization consistently applies to the higher meso- and macroscopic scales of ordering and thus governing the materials properties. However, truly spontaneous behaviour, statistically speaking, is impossible to reach a consistent pattern of assembly. This self-assembly phenomena apply to both animate and inanimate creatures (see Figure 1). Self-assembly, self-organisation, and self-synthesis phenomena were first observed in natural system by molecular biologists in DNA, which were then followed by chemists and materials scientists to synthesize supramolecular structures and fabricate advanced materials⁴.

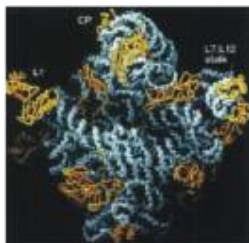


Fig 1. Self-Assembled Molecule of RNA³.

Self-assembly and self-organization are the terminologies popularly used for self-processes in matter. They behave as programmed systems and spontaneously generate well-defined, organized functional structure/architecture at supramolecular level in equilibrium conditions⁴. Self-assembly covers a full range of self-processes and scales (nano-, meso-, and macrolevel), and it is led by interaction algorithms which involves three stages⁵:

- (1) Internal organization: self-recognition, self-selection, and self-assembly;
- (2) Functional self-integration and operation: self-regulation, self-wiring, self-transformation, and self-replication; and
- (3) External interaction: self-connection.

Supramolecular chemistry can lead to molecular self-assembly through non-covalent bonds: Hydrogen bonds (H-bonds), coordination bonds, hydrophobic interactions, electrostatic, and van der Waals interactions⁶. Among these bonds, the synthesis and self-assembly of polyurethanes can benefit from H-bonds between urethane, hydroxyl, and urea groups. Like all other non-covalent bonds, the energy of H-bonds is much weaker than that of covalent bonds (see Table 1).

Table 1. Bonding Strength (kJ/mol) of Functional Groups ⁶

No.	Bonds	Group	Strength
1	Covalent	H – H	436
2		O = O	498
3		N ≡ N	945
4	H-bonds	OH -- N	29
5		OH -- O	21
6		NH -- N	13
7		NH -- O	8

2. Nanostructure Self-Assembly in Polyurethane Nanocomposites

Flexible copolyurethane-urea foams observed in this study have a unique structure assembled by hydrogen-bonds between adjacent urea groups (see Fig. 2). Both hydrogens of each urea group can form H-bonds (bidentate urea), but in nanocomposite cases the second H-bonding of monodentate urea groups was hindered. The H-bonds held together polyurea blocks to form the hard-phases of polyurethane foams structure. Rapid formation of H-bonded bidentate urea, and hence hard-phases of polyurethane foams, marked the onset of structure assembly: microphase separation transition (MST). This assembly of hard- and soft-microphases was in turn followed by structural assembly at higher level. The assembly of three-dimensional structure of foam cells and struts was triggered by the CO₂ blowing⁷.

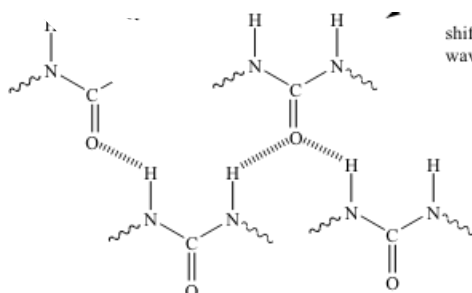


Fig 2. H-bonding induced assembly of polyurethane foam nanostructure⁷.

The nanoscale supramolecular structure of polyurethane foams is mainly governed by H-bonding between urea groups. The formation of this functional group can be analyzed using FTIR instrument, since mid range infrared is particularly sensitive to the covalent bond vibrations of functional groups. Lower frequency of covalent bond vibration indicates a weak interaction of the functional group with other adjacent group⁴.

In Fig. 3, soluble urea is formed initially and its concentration increases steadily. Adjacent urea multiblocks start to interact via H-bonds (mono- & bidentate) then assemble into hard phases. Microphase separation transition (MST) defines the onset of rapid evolution of hydrogen-bonded ureas, and hence the self-assembly of supramolecular structure⁴.

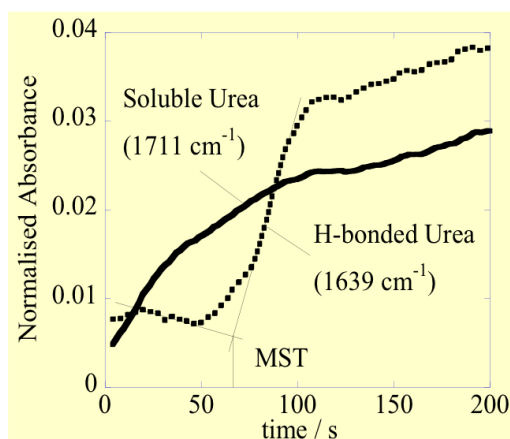


Fig. 3. Microphase separation transition (MST) marked the onset of structure assembly in polyurethane⁷

The presence of nanofiller, like layered-silicate (nanoclay), influences bubble nucleation and coalescence. Layered-silicate filled foams tend to have smaller cells with relatively more uniform sizes⁷. As seen in Fig. 4, this micrograph shows orientation of the nanofiller, indicating a strong interaction between the layered-silicate and foam formulation. The addition of layered-silicate may distribute the surface tension of bubbles, and hence lowering the occurrence of bubble coalescence. It is clear that the presence of a molecular scale ingredient brings about an additional rule of assembly to the reacting mixture, resulting in a relatively better organized structure.

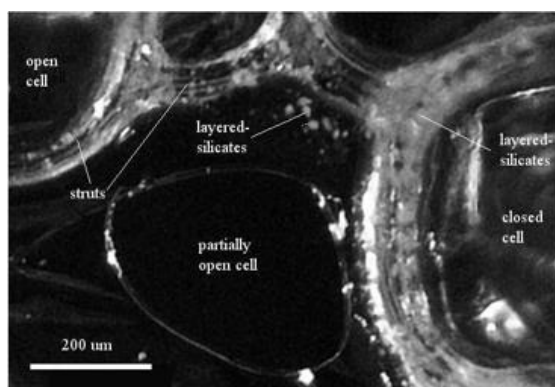


Fig. 4. Micrograph of polyurethane foam, showing filler orientation within struts⁷

Because of this edge-to-edge orientation of the nanofillers, the self-assembly of nanostructure in terms of microphase separation is interfered. Although MST as indicated by the first hydrogen bonding to form monodentate urea is accelerated by the catalytic nature of nanoclay, apparently it retards the second hydrogen bonding of urea group, leaving a lower amount of bidentate urea formed⁷.

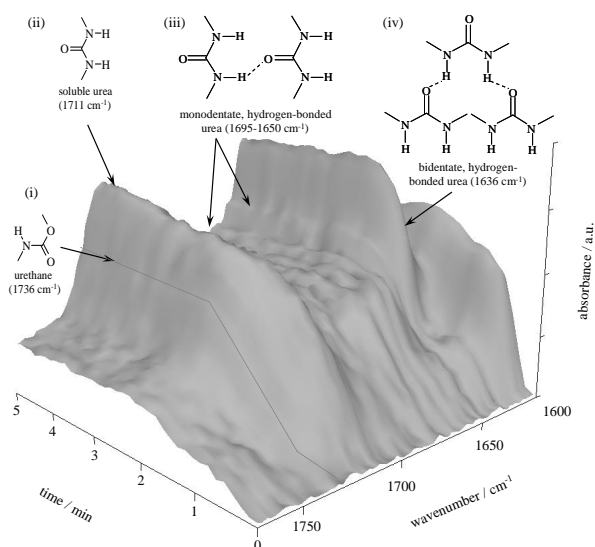


Fig. 5. A typical series of time-resolved FTIR spectra in the carbonyl (C=O) region for unfilled foam with band assignments (i) – (iv) as indicated, reproducible for four replicates⁷.

After 9 minutes of reaction, two dimensional spectra were analysed as presented in Figure 6.

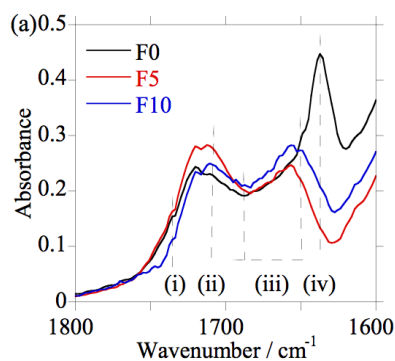


Fig. 6. Comparative spectra in the carbonyl region of unfilled (F0) and natural Montmorillonite-filled (5 & 10% w/w) flexible Polyurethane foams, after 9 minutes of reaction. Stretching band assignments are shown for: (i) free urethane (1736 cm^{-1}); (ii) soluble urea (1711 cm^{-1}); (iii) monodentate, H-bonded urea (1695-1650 cm^{-1}); and (iv) bidentate, H-bonded urea (1636 cm^{-1}).

Fig. 6 clearly shows that there is an appreciable spectral shift (61-75 cm^{-1}) from bidentate to monodentate urea induced by unmodified nanoclay (microscale), indicating shorter yet stronger hydrogen bonds⁷. However, the formation of bidentate urea was not retarded when the montmorillonite nanofiller was organically-modified (nanoscale). The formation of urethane was increased however, due to additional OH group introduced by the organic modifier, as seen in Figure 7.

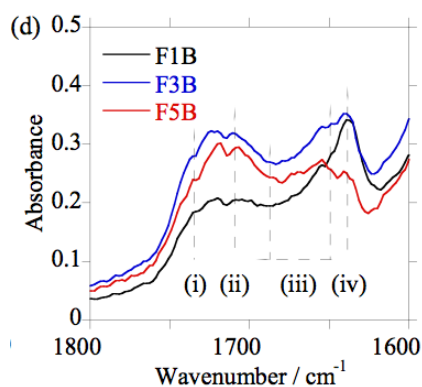


Fig. 7. Comparative spectra in the carbonyl region of organically modified Montmorillonite-filled (1, 3, 5 % w/w) flexible Polyurethane foams, after 9 minutes of reaction. (Stretching band assignments are as stated in the caption of Fig. 6)

BARRIER PROPERTIES ENHANCEMENT IN POLYURETHANE NANOCOMPOSITES

Self-assembly during the structure development of materials may tune their barrier properties⁸. Molecular structure and intermolecular interaction affect barrier properties of materials⁹. One important barrier property is fire retardancy. Just like that for barrier properties, self-assembly of molecular structure will also affect fire retardancy of materials.

1. Roles of Nanofillers in Fire Retardancy Enhancement

There are two main types of flame retardants for polymers: the additives and the reactive types². Examples of fire retardant additives for polymer nanocomposites are phosphorus-containing, halogen-containing, silicon-containing, metal hydrate or oxide. The use of additive type flame retardants may cause a variety of problems to arise, such as poor compatibility, leaching, and a reduction in mechanical properties².

The application of reactive flame retardants, like nanocomposite formulation, involves either the design of new, intrinsically flame-retarding polymers or modification of existing polymers through copolymerisation with a flame-retarding unit either in the chain or as a pendant group. It lacks sufficient versatility in manufacturing, processing and is uneconomical, due to the expense associated with developing a new material for use. However, results show that the incorporation of even a few weight percent of the unit into the polymer chains can lead to remarkable improvements in the overall flame retardancy of the polymer².

More of functionalised nanoclays are used in many fire retardant polymer nanocomposites because they can improve flammability properties^{10,11}. Hindered amines are used to modify the nanoclay effectively, that as low as 1-5% inclusion of the nanofillers will reduce 70-80% peak heat release rate from burned samples^{11,12}. The improved flammability properties is due to the differences of condensed phase decomposition processes induced by the nanofillers interactions with polymer matrix¹².

Other nanofillers used to enhance fire retardancy in several polymer materials include carbon nanotubes. An nanofiller interconnected network layer was formed during combustion, which insulated the polymer from external radiant flux by one half and changed heat transfer from conduction to radiation, as well as increased the melt viscosity which prevents dripping and flowing of the nanocomposites during combustion, resulting in a decrease in Loss of Ignition (LOI)¹. Polyhedral oligomeric silsesquioxane (POSS) is another flame retardant explored¹. Its benefits during combustion include accumulation of a ceramic layer on the surface of the burning materials by thermal degradation of POSS. The layer serves as a physical protective barrier that can strongly

decrease the combustion rate.

Other methods of reactive flame retardation include grafting and coating techniques². Grafting techniques is a novel approach to improve the flame resistance of polymers and compatibility of the polymer with additive flame retardants. It was also found that saponification after grafting can promote char formation and further enhance the flame retardancy². However, it was demonstrated that improvement of the fire properties of the composites has been achieved to the detriment of mechanical properties, which are strongly affected by the presence of the grafted monomer, in this case brominated monomer². Coating technology is an economical and effective way to modify the surface of materials. Usually 5% of the total weight contributes to the coating. The coating can significantly help reduce the water sensitivity and adjust the polarity and hence improve the compatibility during extrusion of polymer².

2. Nanofillers and Barrier Properties Enhancement in Polyurethane Nanocomposites

There was hypothesis on fire retarding activity of nanofiller, for instance montmorillonite or other aluminosilicates, that it is based on gasification and precipitation of the nanofiller². It is considered that when polymer matrix is gasified or burned away, the nanofiller foils remain and accumulate or precipitate at the surface of degrading matrix thereby providing a barrier to oxygen diffusion and flame transfer into the underlying polymer and of volatiles out². This enrichment in nanofiller concentration occur above the glass transition temperature and would be temperature dependent. The ignition time, ignition temperature, rate of heat release, and other flammability characteristics were affected². Substitution of Al or Si atoms with Fe in the clay can act as a radical trap and hence slow down the rate of combustion².

Research indicates that while nanoclays present in polymers nanocomposites slow down burning and provide evidence of char-enhancement, they do not reduce ignition tendency or reduce after-flaming properties². Therefore they will require to act with other flame retardants at reduced concentration to successfully yield up to UL94 V-0 ratings².

Liggat *et al.* patented in 2006 formulation, preparation, and uses of fire retardant flexible polyurethane foam¹³, incorporating partially and/or totally exfoliated nanoclay. Char promoting agent was used, as well as fire retardant and coupling agent. The use of coupling agent is to control the viscosity of polyol matrix by orienting the clay particles into face-to-face alignment, rather than face-to-edge. Almost self extinguishing formulation was achieved at the addition of 8% Cloisite 30B (exfoliated nanoclay) and 30% melamine (fire retardant). Desirable mechanical properties of foam material were retained.

CONCLUSIONS

The incorporation of nanofillers in polymer nanocomposites affect the their mechanism of nanostructure self-assembly, and in turn will influence their barrier properties, especially fire retardancy. In the case of montmorillonite / flexible copolyurethane-urea foam nanocomposites, the scale of nanofiller significantly affects their nanostructure. The nanoscale filler (organically-modified montmorillonite) results in nanocomposite foams with enhanced barrier properties and fire retardancy, while maintaining their flexibility.

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REFERENCES

- [1] Gilman, JW, Jackson, CL, Morgan, AB, Harris, R, Manias, E, Giannelis, EP, Wuthenow, M, Hilton, D, Phillips, SH. (2000) *Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites*, Chemistry of materials, 12(7), 1866-1873.
- [2] Zhang, Sheng, Horrocks. A. Richard. (2003), *A review of flame retardant polypropylene fibres*, Progress in Polymers Science, 28, 1517–1538.
- [3] Whitesides, G.M. (2002) *Self-Assembly at All Scales*, Science, 29, 2418-2421.
- [4] Fithriyah, N.H. (2012). *'Self-Assembly' in the Development of Polyurethane Structure: A Sign of Subservience to Allah*. Proceedings International Seminar on Integrating Islam and Knowledge, Surakarta, Indonesia.
- [5] Lehn, J. M.. (2002) *Toward complex matter: Supramolecular chemistry and self-organization* PNAS. 99(8), 4763–4768.
- [6] Chandrasekhar, V.(2007) *Supramolecular and Self-Assembly Materials*. Proceedings IITK REACH Symposium, Timber Trail
- [7] Fithriyah, N.H. (2009) *Structure Development of Layered-Silicate / Flexible Polyurethane Foam Nanocomposites*. PhD Thesis, The University of Manchester.
- [8] Bharathi, S, Nogami, M, and Ikeda, S. (2001) *Novel Electrochemical Interfaces with a Tunable Kinetic Barrier by Self-Assembling Organically Modified Silica Gel and Gold Nanoparticles*. Langmuir, 17(1), 1–4.
- [9] Jennings, G.K., Yong, T-H., Munro, J.C., and Laibinis, P.E.(2003) *Structural Effects on the Barrier Properties of Self-Assembled Monolayers Formed from Long-Chain ω -Alkoxy-n-alkanethiols on Copper*. J. Am. Chem. Soc., 125(10), 2003, 2950–2957.
- [10] Gilman, J, Kashiwagi, T, Lichtenhan, J. (1997), *Nanocomposites: a revolutionary new flame retardant approach*. SAMPE Journal, 33, 1997, 40–6.
- [11] Gilman JW, Kashiwagi T, Lichtenhan J. (2001) *Recent advances in flame retardant polymer nanocomposites*. Proceedings of Conference on Fire and Materials, London: Interscience Communications, 2001, pp. 273 – 84.
- [12] Gilman, JW. (1999) *Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites*, Appl Clay Sci, 15(1–2), 31 – 49.
- [13] Liggat, J., Pethrick, R.A., Rhoney, I. (2006) *Fire retarded flexible nanocomposite polyurethane foams*, WO 2006003421 A1, 2006