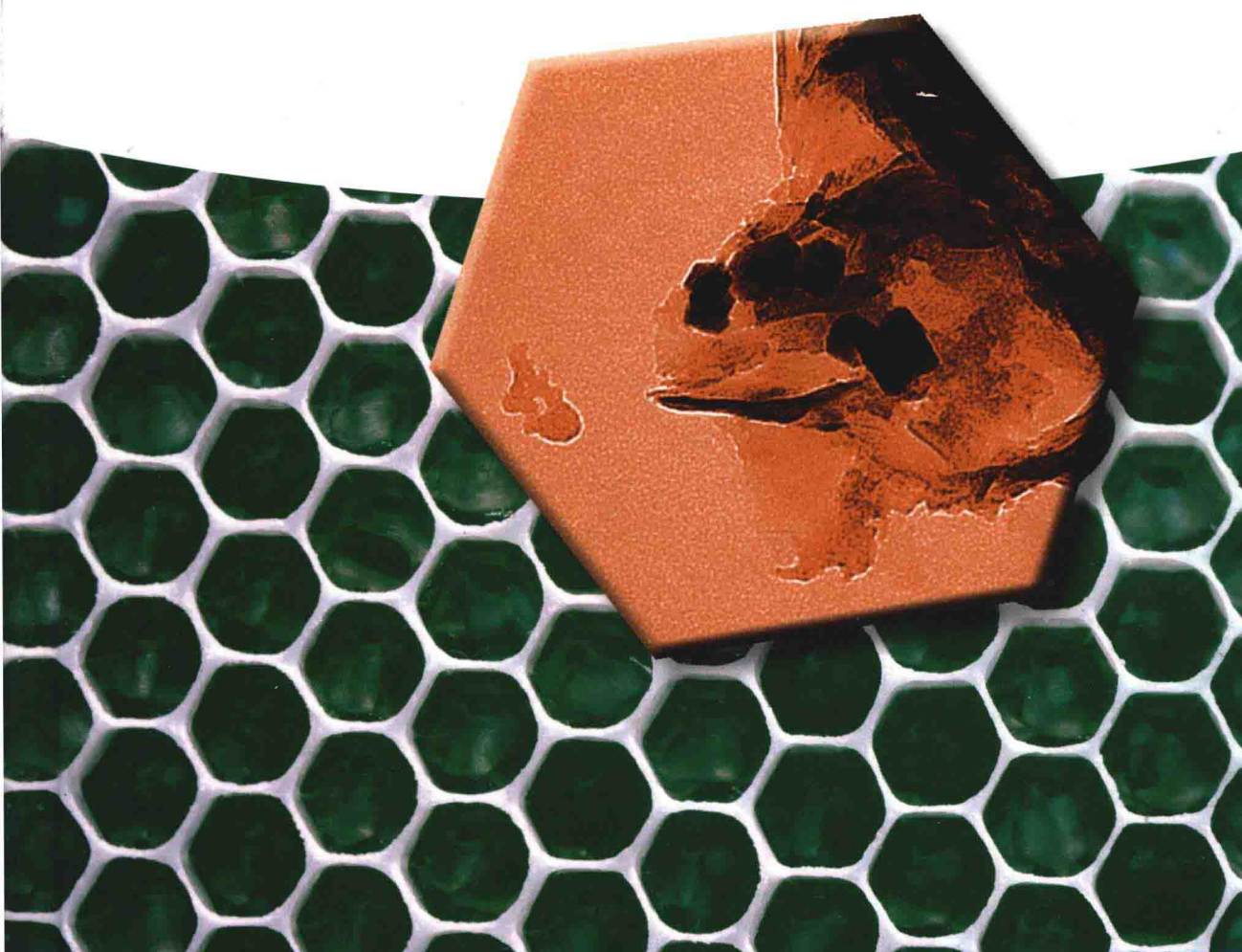


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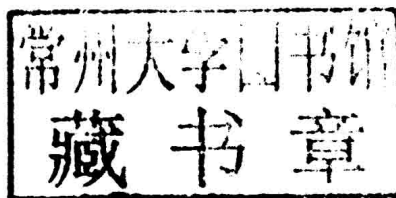
Thermoset Nanocomposites



Polymer Nano-, Micro- & Macrocomposites

Edited by Vikas Mittal

Thermoset Nanocomposites



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Preface

Thermoset polymers are an important class of materials with many superior properties as compared with thermoplastic materials. Generation of thermoset polymer nanocomposites by the incorporation of layered silicates and other nanofillers in the polymer matrices has led to enhancement of the property profiles of the thermoset materials significantly. Nanocomposites with a large variety of thermoset polymers have been explored, and vast knowledge on the synthesis methodologies as well as properties has been generated. The goal of the book is to assimilate these research findings on many thermoset polymer-based nanocomposite systems comprehensively so as to generate better insights into the design, performance, and optimization of thermoset nanocomposites.

Chapter 1 reports the synthesis and properties of epoxy vermiculite nanocomposites. Vermiculite platelets were surface modified to enhance interfacial interactions with the polymer, and the nanocomposites were generated using *in situ* polymerization method. Interesting insights into the permeation properties of the nanocomposites have been reported. Chapter 2 presents photoinduced polymerization as an efficient technique for rapid formation of highly cross-linked networks from liquid epoxy resins. The reaction involves a cationic mechanism and is usually initiated by UV light. Chapter 3 reports the synthesis and properties of polyurethane (PU) nanocomposites, and it was observed that the key to superior properties of nanocomposites is critically dependent on the choice of the organic modifier used to modify the surface of clay as well as the nature of the polymer itself. Chapter 4 reviews recent progresses on thermal properties of formaldehyde-based thermoset/cellulose nanocomposites such as melamine-formaldehyde (MF) resin/clay/cellulose, phenol-formaldehyde (PF) resin/clay/cellulose, or PF resin/multiwalled carbon nanotube (MWCNT)/cellulose nanocomposites, particularly by focusing on thermal curing or degradation kinetics of these nanocomposites. Chapter 5 reports a review of mechanical properties of thermoset polymer nanocomposites. It is reported that the nanoclay particles provide to thermosets interesting mechanical properties when the constituents and the processing parameters are adequately selected. These properties are highly improved in the case of rubbery matrix than in glassy matrix. Chapter 6 demonstrates the unsaturated polyester clay nanocomposite systems. These composites are of high importance as the unsaturated polyester resins are the most widely used thermoset matrix

resin in the coatings and composites industry, and constitutes about three-fourth of the total resins used. In Chapter 7, recent advances on applications of hyper-branched polymers as clay surface modifications are presented, with particular reference to the preparation of antimicrobial surface and adsorbents for Cr (VI) water treatment. Chapter 8 focuses on new methods to generate metal- and clay-reinforced nanocomposites. The development of *in situ* methods has clearly facilitated the major advances in the synthesis in a one-pot manner combining polymerization processes leading to the network formation with intercalation/exfoliation or nanoparticle formation, respectively. In Chapter 9, the preparation and properties of the bio-based epoxy resin/hardener/layered silicate nanocomposites are described. The replacement of petroleum-based epoxy resin/hardener with bio-based epoxy resin/hardener is very important from the viewpoint of the conservation of limited petroleum resources and the protection of global environment. In Chapter 10, comprehensive account of electrical and electromagnetic interference (EMI) shielding properties of thermosetting nanocomposites has been provided with special reference to those based on conducting additives like intrinsically conducting polymers and carbonaceous fillers like carbon nanotubes and graphene.

Abu Dhabi
June 2013

Vikas Mittal

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1

Epoxy–Vermiculite Nanocomposites*Vikas Mittal***1.1****Introduction**

Epoxyes form a special class of thermosetting polymeric materials having high thermal and environmental stability. They are well known as creep-resistant materials with very high stiffness properties [1–3]. Owing to these properties, a wide spectrum of epoxy applications is available, which includes the use of epoxyes as adhesives, coatings, printed circuit boards, electrical insulators, and so on. One of the major areas where epoxy adhesives find tremendous use are packaging laminates where their sole use is to hold together the various polymeric foils used in these commercial packaging laminates. To save the material costs, an overall decrease in the thickness of the packaging laminate can be achieved if the adhesive can also be made to contribute to the properties required for a packaging material apart from its function of being an adhesive. The common properties required being the permeation barrier, mechanical performance, transparency, suitability for food contact applications, ease of printability, and so on. Permeation barrier to oxygen and water vapor form the most important property needed in the packaging materials. This can be achieved by altering the polymer network structure obtained by crosslinking of the epoxide groups with amines or other crosslinking agents [4, 5]. The use of epoxy polymer with stiff rod-like units in the backbone can help to enhance the required properties. The other alternative includes the incorporation of inorganic fillers in the polymer matrix, this approach being easier to monitor and control. As the filler shape, size, and interfacial interactions affect the polymer properties greatly, organically treated plate-like inorganic aluminosilicate particles can be incorporated in the polymer matrix to achieve polymer nanocomposites for improvement in barrier performance. By incorporating impermeable, transparent, plate-like nanoparticles in the polymer matrix, the permeating molecules are forced to wiggle around them in a random walk, hence diffusing through a tortuous pathway [6–8]. Besides, the decrease in transmission rate of the permeant is a function of the aspect ratio of the inclusions, their volume fraction, and orientation.

The synthesis of epoxy–clay nanocomposites has been extensively studied; however, majority of these studies focused on enhancing the mechanical properties

with the incorporation of organically modified fillers [9–17], thus largely neglecting the permeation properties. Only a few recent studies have discussed these properties in detail [18–23]. Apart from that, montmorillonite has been the most commonly used aluminosilicate in these studies. Owing to the low charge density ($0.25\text{--}0.5\text{ equiv mol}^{-1}$), a larger area per cation is available on the surface, which leads to a lower basal plane spacing in the clay after surface ion exchange with alkyl ammonium ions. On the other hand, minerals with high charge density (1 equiv mol^{-1}), such as mica, and hence subsequent smaller area per cation, do not swell in water and thus do not allow the cation exchange. However, aluminosilicates with medium charge densities of $0.5\text{--}0.8\text{ equiv mol}^{-1}$, such as vermiculite, offer a potential of partial swelling in water and cation exchange, which can lead to a much higher basal plane spacing in the modified mineral if optimum ion exchange is achieved. In the pristine state, vermiculite particles are composed of stacks of negatively charged 2:1 aluminosilicate layers (ca. 0.95 nm thick) with one octahedral sheet sandwiched between two opposing tetrahedral sheets and the resulting regular gap in between (interlayer). The chemical constitution of its unit cell is $(\text{Mg,Al,Fe})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2\text{Mg}_x(\text{H}_2\text{O})_n$ [24, 25]. Due to isomorphic substitutions in the lattice, the layers have permanent negative charges that are compensated mainly by hydrated Mg^{2+} as interlayer cations. Owing to the higher basal plane spacing in the modified mineral, the electrostatic interactions holding the layers together can be expected to be lower than similar montmorillonite counterparts thus increasing the potential of better properties of the hybrid nanocomposites.

The goal of this investigation was to synthesize epoxy-vermiculite nanocomposite coatings and to study their microstructure development as well as their oxygen and water vapor barrier properties in comparison with already reported epoxy-montmorillonite system [18]. Vermiculite platelets modified with two different ammonium ions were prepared for the purpose. The epoxy matrix and the curing agent were chosen to achieve polymer matrix, which meets the requirements of the food and health regulations and has low gas permeability on its own. The nanocomposite coatings were drawn on polyamide and polypropylene substrates and the curing temperatures were kept low in order to avoid the thermal damage to these substrate foils.

1.2

Experimental

1.2.1

Materials

The epoxy resin, bisphenol A diglycidyl ether (4,4'-isopropylidenediphenol diglycidyl ether) with an epoxide equivalent weight $172\text{--}176$, was supplied by Sigma (Buchs, Switzerland). Tetraethylenepentamine (TEPA) and tetrahydrofuran (THF) were procured from Fluka (Buchs, Switzerland). Benzyltrimethylhexadecylammo-