

CHAPTER II

LITERATURE REVIEWS

In recent years, polymer-clay nanocomposites have gained wide interest by many researchers because the materials allow significant improvement in their physical properties, such as mechanical strength, heat deflection temperature, and thermal expansion coefficient (CTE). In addition, many inorganic minerals can reduce manufacturing cost since most of them are inexpensive.

Usuki et al. (1993) and Okada et al. (1995) prepared nylon 6-clay nanocomposites by *in-situ* polymerization of ϵ -caprolactam in organophilic-clay. The natural sodium-montmorillonite was cation exchanged with various ω -amino acid and concentrated hydrochloric acid. Transmission Electron Micrograph (TEM) revealed that the silicate layers produced a fine dispersion in polymer matrix. A slight addition of 2 % weight of clay in nylon 6 showed twofold improvement in tensile modulus as compared to an untreated nylon 6. The timing belt cover which was produced from this nanocomposite exhibited good rigidity with an excellent thermal stability.

Kojima et al. (1993) have successfully prepared a nylon 6-clay hybrid in one-pot synthesis by polymerization of ϵ -caprolactam, phosphoric acid, and 6-amino-caproic acid in the presence of natural sodium-montmorillonite. The tensile strength, modulus, and heat deflection temperature of the composites increased with increase clay content. The results were close to the conventional preparation method as reported by Usuki et al. (1993).

Yano et al. (1993) prepared flexible polyimide-clay hybrids using a solution-casting method. The organophilic-clay was uniformly dispersed in a polyimide film. The hybrids or nanocomposite material exhibited excellent gas

barrier properties and a lower thermal expansion coefficient compared to an untreated polymer.

Messersmith and Giannelis (1995) prepared poly(ϵ -caprolactone)-clay nanocomposites using 12-aminododecanoic acid together with concentrated hydrochloric acid as a cation exchanging reagent in sodium-montmorillonite. Wide-Angle X-ray Scattering (WAXS) patterns of the composite showed no discernable reflections below $2\theta = 10^\circ$. The results suggested that the alumino-silicate layers produced fine dispersion in polymer matrix. The nanocomposites also exhibited a significant reduction in moisture permeability.

Pinnavaia et al. (1996) prepared epoxy-clay nanocomposites by *in-situ* polymerization of epoxy resin monomer in different types of organophilic-clay. Both the tensile strength and modulus increased with increase clay content.

Giannelis (1996) prepared poly(ethylene oxide)-clay nanocomposites by direct intercalating polymer melt, above its glass transition temperature, into sodium-montmorillonite and lithium-montmorillonite. Differential Scanning Calorimetry (DSC) traces revealed that the silicate layers suppressed crystallization of the polymer chains. Giannelis et al. (1995) also investigated the kinetics of polystyrene melt intercalation in organophilic-clay using the WAXS measurements and TEM to monitor the changes of basal spacing in silicate layers during the intercalation process. The rate of conversion was determined at various temperatures and various molecular weights of polystyrene. The result indicated that the activation energy of intercalate formation was close to self-diffusion of ordinary polymer chains in the bulk melt. This implied that the polystyrene-clay intercalation requires no additional processing time.

Ogata et al. (1997) prepared poly(*l*-lactide)-clay nanocomposites using chloroform as a co-solvent in the preparation process. The SAXS and WAXS patterns indicated that the organophilic-clay showed no fine dispersion in the composites. The DSC curves indicated that the organophilic-clay can act as a nucleus for polymer crystallization. The silicate layers existed in the form of tactoid which was composed of several silicate monolayers. The tensile modulus of the composites also was improved like the previous studies of other polymer-clay nanocomposites.

The nanocomposites research has now expanded into developing of novel ceramic and cermet materials. Niihara (1991) prepared a nanocomposite of silicon carbide in a fine-grained polycrystalline alumina. The material allowed significant improvements in CTE as compared to an original ceramic. Baraton et al. (1996) synthesized a nanostructure of aluminum nitride powder *via* sol-gel technique and has successfully characterized this material using the FTIR, TEM and WAXS. The piezoelectric Al₂O₃/PZT-PMN-MnO₂-NiO nanocomposite has also been studied by Newnham and Trolier-McKinstry (1990). The material showed improvements in mechanical Q-factor and electromechanical coupling coefficient. Chow et al. (1989) demonstrated the co-deposition of silica and metal alloys producing a nanoscale composite coating of silica fiber in a metal matrix.

The wide variety of nanoparticles in polymeric materials have been studied by many researchers, such as Bronstein et al. (1994) who synthesized a copolymer of polyacrylonitrile (PAN) in the presence of W-, Mo-, and Cr-carbonyl complexes. The nanoscale material of cobalt in PAN was prepared by mixing the powder of Co₂(CO)₈ with the PAN copolymer in dimethylformamide as the solvent and followed by heating up to 220 °C. The ferromagnetic resonance and SAXS pattern revealed that the average size of cobalt particles were varied from 1 to 10 nm.

The polymer-ceramic or polyceram nanocomposites *via* sol-gel technique have been of interest to many researchers in recent years because the material can be produced at low temperature conditions and the properties of that material are usually better than achievable by the simple mechanical blending of inorganic filler and polymeric material. Typically, the polycerams can be classified into three classes as described by Morikawa et al. (1992). In *Class I*, the sol-gel reaction proceeds in a solution of linear polymer. The polymer chains may contain one or more functional groups that can react with the metal oxides. In *Class II*, the sol-gel reaction proceeds in a solution of cross-linked polymer. In *Class III*, the sol-gel reaction proceeds during the polymerization of monomers in metal oxides. Recently, Klein and Woodman (1995) prepared a nanocomposite of poly(vinyl acetate) bonding together with silicon alkoxide *via* sol-gel technique and investigated the effect of formamide substitutions. Time to gel, skeleton density, and their linear shrinkage allowed significant affect on the presence of formamide. Another example given for polyceram materials is polyimide-silica hybrids as produced by Mascia and Kioul (1995). The morphology of this material was controlled by small amount additional of γ -glycidyoxypropyltrimethoxy silane. The hybrid materials exhibited significant improvements in their thermal behaviors and mechanical properties, such as tensile strength and percent elongation at break.