

CHAPTER I

INTRODUCTION

Polymers in their combination with various additives and fillers are popular materials for making household articles or used directly as construction and engineering materials. Usually, polymers are filled with crystalline minerals, a class of materials called polymeric composites. Composites are heterogeneous substances consisting of two or more materials which do not lose the characteristics of each component. This combination of materials brings about new desirable properties. Industrially, mineral filler additives are added into the polymer matrix not only to reduce the cost, but also to improve other properties, such as mechanical properties, dimensional stability, and surface hardness. The effect of fillers on mechanical and other properties of the composites depends strongly on their shape, size and size distribution of the primary particles and their aggregates, surface characteristics, and degree of dispersion.

Of the various mineral fillers used, calcium carbonate (CaCO_3) is the most common one, due mainly to its availability in readily usable form and low cost. However, the incompatibility of its high energetic hydrophilic surface with the low-energy surface of hydrophobic polymers, such as polyethylene (PE) and polypropylene (PP), is a problem to be solved before it can be used as a functional filler. For this and other reasons, the surface of calcite is often rendered organophilic by a variety of surface modifiers such as silane, titanate, phosphate, and stearic acid. Commonly, stearic acid is the most common surface modifier, while use of other types seem to be limited by their relatively high cost. One question regarding the efficiency of stearic acid as the surface modifier for improving adhesion and dispersion between CaCO_3 and the polymer matrix is the level of its compatibility with the matrix molecules.

On the basis of "like dissolves like," the interfacial interaction (adhesion) between materials of a similar chemical nature is considered superior to that of any other type. Let us imagine if there is a technology that can put a thin layer of the matrix material to act as the surface modifier for CaCO_3 , what would be like for the surface-modified CaCO_3 to perform in the matrix? In fact, one such technique,

admicellar polymerization, has been developed. Admicellar polymerization technique is based on physically adsorbing surfactants onto a substrate. Nevertheless, at right conditions, the admicellar layer adheres well to the substrate via ionic interactions. The structure and properties of such an ultrathin organic film have a strong influence on the final properties of the composites because this film represents the interface between the two phases that are heterogeneous in nature. It also determines the particle-particle as well as the particle-matrix interactions and controls the buildup of the interphase.

In this study, the admicellar polymerization technique is used to produce ultrathin polypropylene film on the surface of CaCO_3 particles. The film-forming process includes four major steps: (i) the adsorption of a thin admicellar layer of surfactants, e.g. sodium dodecylsulfate (SDS), on CaCO_3 substrate; (ii) the adsolubilization of propylene gas monomer into the admicelles; (iii) The initiation of polymerization within the admicellar bilayers; (iv) the washing of the treated CaCO_3 to remove as much of the outer surfactant layer as possible in order to expose the film. The purpose of this study is to investigate the effect of CaCO_3 particles of various surface characteristics (i.e. untreated, admicellar-treated, and stearic acid-treated) on mechanical properties of CaCO_3 -filled isotactic polypropylene composites.

1.1 Theoretical Background

1.1.1 Admicellar Polymerization

The admicellar polymerization, *in-situ* polymerization reaction of organic monomer in the hydrophobic region of a surfactant bilayer adsorbed onto the surface of suspended particles in water. This is a novel method for applying an ultra thin polymeric film on a substrate surface. The most significant advantage of this technique relatively to other methods is the ability to apply a very thin layer on the substrates.

The thin-film polymerization process can be envisioned as occurring in four major steps: admicelle formation, monomer adsolubilization, *in-situ*

polymerization of adsorbed monomers, and surfactant removal as illustrated in Figure 1.1.

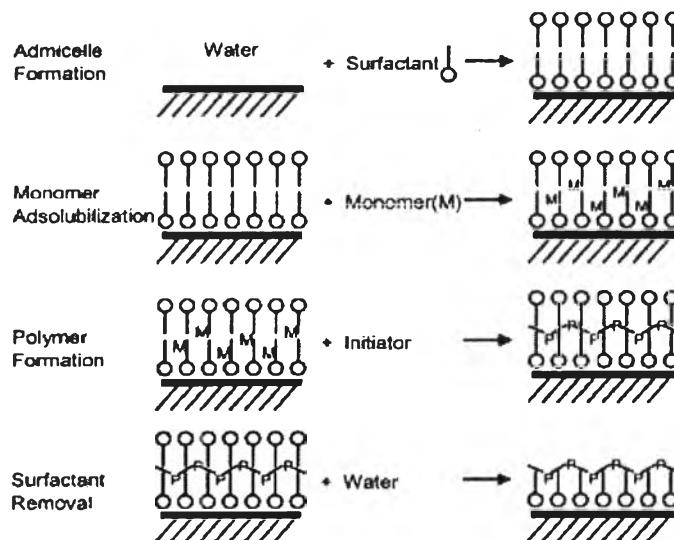


Figure 1.1 Schematic of four steps admicellar polymerization process.

Step 1: Admicelle Formation

The aggregation of surfactants at solid/liquid interfaces to form bilayers (admicelles) through adsorption from an aqueous solution is a well-known phenomenon. For the adsorption of ionic surfactants on a solid surface, the adsorption isotherm curve is typically an S-shaped when one plots the logarithm of adsorbed surfactant versus the logarithm of equilibrium concentration of surfactant. The S-shaped isotherm can be separated into four regions as shown in Figure 1.2. In region I, surfactant adsorption is mainly by ion exchange and the amount of surfactant adsorption increases linearly with an increase in surfactant concentration. In region II, there is a marked increase in the slope of the graph resulting from interaction of the hydrophobic chains of oncoming surfactants with those previously adsorbed to form admicelles, bilayer aggregates, on the solid surface. In region III, the slope of the isotherm is reduced because adsorption now must overcome electrostatic repulsion between the oncoming ions and the ionic head groups of the surfactants on the surface. Surfactant surface coverage can be limited either by the attainment of the critical micelle concentration (CMC) below bilayer coverage at low

surface charge densities or by the attainment of bilayer coverage below the CMC at high surface charge densities. In either case, the adsorbed surfactants reach equilibrium in region IV where the amount of surfactant adsorption remains constant with further increase in the surfactant concentration.

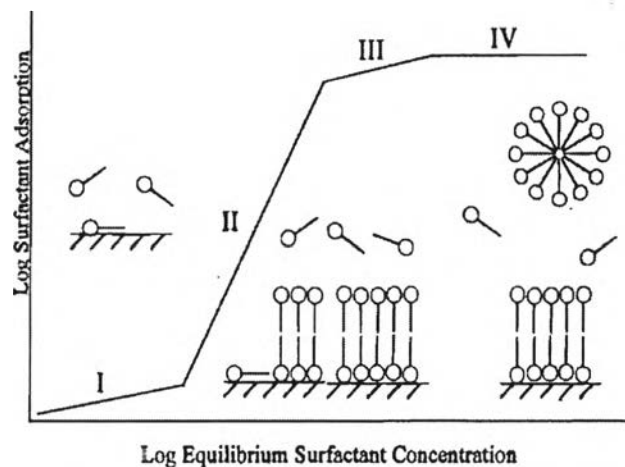


Figure 1.2 Typical adsorption isotherm of surfactants on solid surfaces.

To obtain admicelle formation, the most critical parameter to be manipulated is the solution pH, which should be adjusted until the surface exhibits a net surface charge of zero (referred to as the point of zero charge or PZC). At pH values below the PZC, the surface becomes protonated and more positively charged; above the PZC, the surface becomes negatively charged. Consequently, the choice of surfactant is influenced by the PZC of the substrate. That is, anionic surfactants adsorb below the PZC and cationic surfactants above the PZC. In this step, the amount of surfactant required, which is determined from adsorption isotherms, must be lower than the CMC to avoid emulsion polymerization to form within the supernatant liquid.

Step 2: Monomer Adsolubilization

Under conditions favorable for the formation of admicelles on a solid surface and unfavorable for the formation of micelles in an aqueous supernatant, at equilibrium, monomers preferentially partition onto the hydrophobic interior of the admicelles, the process called “adsolubilization.” Formally, adsolubilization can be

defined as the excess concentration of monomers at an interface that would not exist in the absence of admicelles. The organic environment exhibited by the hydrophobic interaction of the amphiphilic tails of the surfactant molecules renders a favorable region to solubilize the organic monomers.

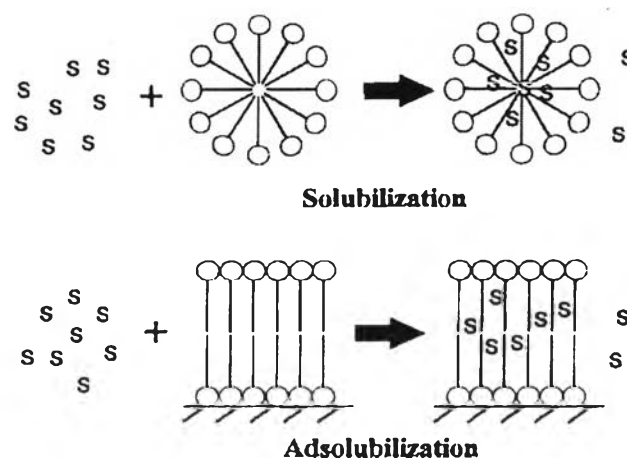


Figure 1.3 The phenomena of solubilization and adsolubilization.

Step 3: *In-situ* Polymerization of Adsolubilized Monomer

In this step, initiator is added to start the polymerization in the admicelle. Water-soluble initiators are generally used and the initiation reaction is started. Once the reaction has begun, additional monomers from the bulk solution diffuses into the micelles. Initiators begin the formation of polymers within the surfactant bilayers, probably by mechanism similar to that occurs in conventional emulsion polymerization, i.e. within micelles. If the reaction continues for a sufficient length of time, essentially all of the monomers dissolved in water will be converted to polymers.

Step 4: Surfactant Removal

After polymerization reaction is complete, the treated substrate, presumably coated with a thin polymeric film, must be washed several times with distilled water to rinse off any residual monomers and surfactants to completely expose the coated film.

1.1.2 Calcium Carbonate (CaCO₃)

Calcium carbonate is one of the earth's most abundant minerals, found in various forms all over the world. It is a very stable mineral, sometimes found in entire mountain ranges in addition to portions of seashores composed of corals and shells. In living organisms, from simple seashells, corals, and mollusks to the most highly-advanced vertebrates, CaCO₃ is an essential mineral that provides structural supports. Skeletal structures containing calcium phosphate as well as CaCO₃.

Owing to the varied geological history of CaCO₃ deposits, many different forms are recognized: they are, for examples, limestone, marble, calcite, chalk, aragonite, and dolomite (calcium-magnesium carbonate). Among these, calcite and chalk, as well as man-made reprecipitated grades, are the most commercially developed forms.

CaCO₃ is the most widely used filler or extender pigment in the plastic industries. Poly(vinyl chloride), polyolefins, phenolics, polyesters, and epoxies are all resins with which CaCO₃ can be compounded. The broad utilization of CaCO₃ is attributed to both economic and performance considerations. CaCO₃ is available at favorable pound-volume costs, and is produced in broad size range and distribution. Current commercial grades include finenesses not available a decade ago, as well as surface-modified grades to promote ease of wetting and dispersion, which permit higher loadings.

In polypropylene, CaCO₃ can be loaded into polypropylene homopolymers and copolymers of as much as 50% by weight (wt.%). Many commercial applications of CaCO₃-filled polypropylene are being found more regularly. Commercially-prepared molding compounds typically contain CaCO₃ particles between 20 to 40 wt.%.