

## CHAPTER II

### LITERATURE REVIEW

Hong et al. (2000) studied the use of color indicators as an active packaging system for evaluating kimchi fermentation. Kimchi fermentation was assessed for titratable acidity (TA), and color changes of the indicators were measured and expressed as Hunter values as well as total color difference (TCD). TCD values of bromocresol purple (BP) type indicator (containing BP as a chemical dye) ranged  $27\pm 33$  and were much more than those of methyl red (MR) type (containing MR). The developed color indicator film consisted of polypropylene (PP) resin, calcium hydroxide as a CO<sub>2</sub> absorbent, and bromocresol purple (BP) or methyl red (MR) as a chemical dye.

Changes in Hunter color values of the indicators within the packages of kimchi. In case of the indicator containing BP, Hunter *L* and *b* values increased gradually with storage time, while Hunter *a* value decreased slowly and then remain constant. However, Hunter *L* and *b* values of the indicator containing MR decreased exponentially, while Hunter *a* value increased remarkably and remained constant. The result meant that color of the BP type indicator turned from initially blue to finally light green, and that of the MR type turned from light orange to red. The rate of the color changes was different depending on temperature but with the same pattern.

Present results suggest that the BP type indicator could be used successfully as a full time-fermentation indicator for kimchi products. However, the MR type might be applied only as a ripeness/unripeness indicator to packaged kimchi because its color change rate nearly reached to zero at the TA values more than 0.7 mg/dl.

Two years later, Hong et al. developed kimchi packaging by using gravure-printed color indicators on common nylon/polyethylene (Ny/PE) film. A gravure process was successfully applied as a novel approach to fabricate color indicators for kimchi packaging. The color changes of the developed indicators properly represented the degree of fermentation of packaged kimchi. These color indicators could be employed as an effective intelligent packaging technology for monitoring ripeness of kimchi products non-destructively.

Supporting by these reviews, the incorporation of indicator dye, such as bromocresol purple and bromothymol blue, into polypropylene could be developed to be pH-sensitive packaging to evaluate milk spoilage.

Those are the literature reviews about indicator dyes incorporated polymer used as a smart packaging. In this work, the organoclay nanocomposite as a nano reinforcement in polymer matrix was also interested due to thermal and mechanical property improvements of polymer.

Bentonite, is the one type of clay that used as a nanofiller in polymer nanocomposite. In 2004, Lee et al. prepared 99% purity montmorillonite-rich clay from Ca-bentonite that mined from Kampo area in Korea. They found that the physical properties such as cation exchange capacity, specific surface area, swelling power, etc. were similar to those of Kunifia-F (Tokyo, Japan). It was found that the exchange weight contents of the organo-surfactants increased with the increasing molecular weight of them. For the same main chain carbon number of surfactants, the exchange contents in mole of primary types were higher than those of the tertiary types. The interlayer distance for MMT-III, HAD-M, ODA-M and ODTMA-M were 1.21, 1.53, 1.57, 2.04, and 2.07 nm. All organobentonites were delaminated in the epoxy matrix forming the epoxy/organobentonite nanocomposites. Tensile strength and Young's modulus increased with the treatment of organo-surfactants and with the increasing clay loading content.

Hasegawa et al. (1998) prepared PP/clay nanocomposites (PPCNs) by using a maleic anhydride-modified PP oligomer (PP-MA) as a compatibilizer. PP was melt blended with organophilic clay (C18-MMT) which was intercalated with PP-MA by twin-screw extruder at 200 °C. In these PPCNs, the particles of silicate layers were dispersed at the nanometer level. The particles become smaller and were dispersed more uniformly, as the ratio of PP-MA to the clay increased. It becomes apparent that PP-MA improved the dispersibility of the clays in the PPCNs. The dynamic storage moduli of the PPCNs were higher than that of PP up to 130°C. As the dispersibility of the clays was improved, the reinforcement effect of the clays increased.

The same authors (2000) also prepared polyethylene-propylene rubber (EPR)/C18-MMT nanocomposites by melt blending EPR-g-MA and C18-MMT

powder using a twin-screw extruder, and then tried to compare the morphology of EPR-based nanocomposites with PPCN.

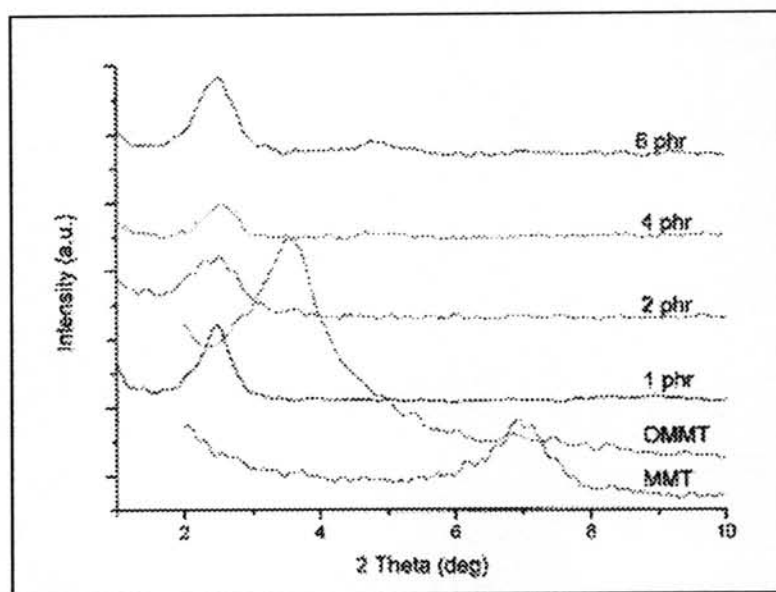
The same year, Manias et al. (2000) reported the preparation by melt intercalation technique of PP/organically modified MMT with both intercalated and exfoliated structures. In order to prepare nanocomposites, they (a) introduced functional groups in PP, and (b) used common alkylammonium MMT and neat/unmodified PP and a semifluorinated surfactant modification for the MMT (f-MMT). For the first approach, they used random copolymers of PP with 0.5 mol% of functionalized comonomers, or diblock copolymers with 1 mol% of non-PP block copolymers. Functional groups that promote nanocomposite formation with dimethyldiallowammonium-modified MMT include *p*-methylstyrene, maleic anhydride, styrene, and hydroxyl-containing styrene; propylene-*b*-methyl-methacrylate diblocks also formed nanocomposites with octadecylammonium-modified MMT. In the second approach, a semifluorinated alkyltrichlorosilane was used to modify octadecylammonium-modified MMT, rendering it miscible with neat PP.

Zhu and Xanthos (2004) investigate the effects of clay chemical modifiers, mixing protocols, and operating conditions upon the clay structure in nanocomposites prepared with a corotating twin-screw extruder. Two mixing methods were used for the nanocomposite preparation: two-step mixing and one-step mixing. Experimental results of MFI show that C15A composites have higher viscosity (lower MFI) than C30B composites. This indicates that C30B was less exfoliated. The mixing protocols have some effects on the MFI of the composites. Generally, in a two-step mixing method, nanocomposites have lower MFI. That is, the composites prepared by the two-step mixing method have better exfoliation for the nanofillers than one-step mixing method.

Tang et al. (2003) studied the influence factors on the thermal stability of PP/montmorillonite nanocomposites. They used two different methods to prepare PPCNs. One was from pristine montmorillonite and a reactive compatibilizer hexadecyl trimethyl ammonium bromide (C16); the other is from different organophilic montmorillonites (OMT). The nanocomposite structure was demonstrated by XRD and TEM. The thermal stability of PPCNs was investigated by TGA. It is shown that

different methods and OMT influence the morphology and thermal stability of PPCNs.

A year later, Ding et al. (2004) studied the effect of the OMMT on the structure and properties of PP. PP/organo-montmorillonite (OMMT) nanocomposites were prepared by using a highly effective PP solid-phase graft (TMPP) as compatibilizer. As a very low amount of PP graft was used. A typical intercalated structure was formed in the composites. The incorporation of silicate layers and TMPP gave rise to a considerable increase in impact strength and flexural modulus compared with the neat PP. The crystallization peak temperature of nanocomposites was about 10 °C higher than that of PP. By adding 4 phr OMMT, the temperature at 5 wt% loss of the nanocomposite was 38°C higher than the neat PP. The Tg of PP was lowered by the incorporation of the OMMT. The changes of the properties could be correlated with the formation of the PP/OMMT nanocomposites.



**Figure 2.1** Effect of OMMT loading on flexural properties of PP/OMMT nanocomposites.

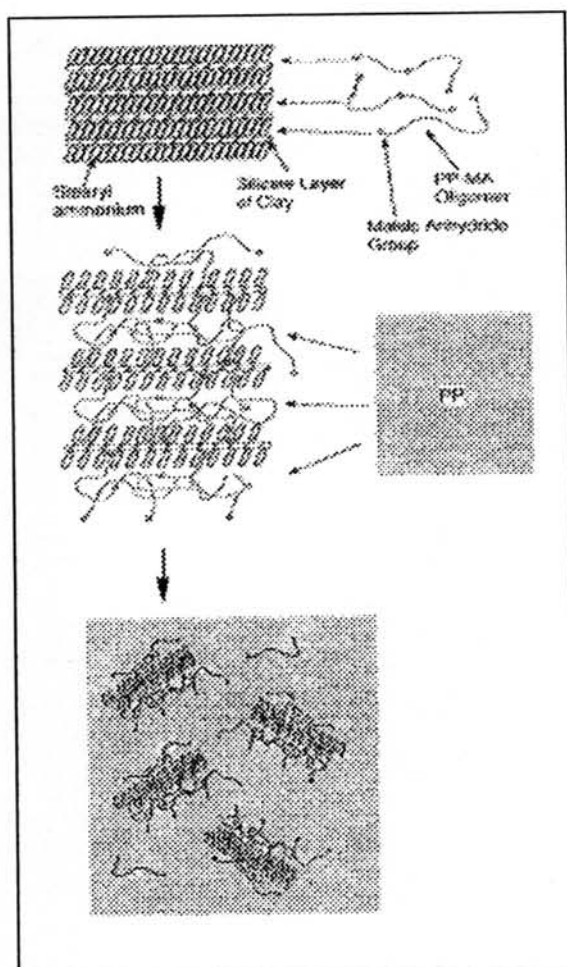
The X-ray diffraction (XRD) profiles of pristine MMT, OMMT, PP, and PP nanocomposites are shown in Figure 2.1. Pristine MMT shows a characteristic diffraction peak at 6.948 corresponding to the 001 plane diffraction. OMMT shows the 001 diffraction peak at 3.628, indicating substantially increased d-spacing of OMMT. However, the d-spacing is independent of OMMT loading.

Thajjaroen (2000) found in case of primary-alkylamine modified montmorillonites (MMTs), the degree of basal spacing expansion was increased with the length of hydrocarbon part in the structure of modifying agents. For quaternary-ammonium salt modified MMTs, the same trend was obtained but the degree of interlayer expansion was lower than that of primary-alkylamine modified counterparts.

Kawasumi et al. (1997) prepared PP/clay hybrids by simple melt-mixing of three components, i.e., PP, maleic anhydride modified PP oligomers (PP-MA), and clays intercalated with stearylammonium. The dispersibility of 10-Å-thick silicate layers of the clays in the hybrids was investigated by using a transmission electron microscope and X-ray diffractometer. It is found that there are two important factors to achieve the exfoliated and homogeneous dispersion of the silicate clay layers in the hybrids. Firstly, the oligomers should include a certain amount of polar groups to be intercalated between silicate layers through hydrogen bonding. Secondly, the oligomers should be well miscible with PP. Since the content of polar functional groups in the oligomers should affect the miscibility of it with PP.

The driving force of the intercalation originates from the strong hydrogen bonding between the maleic anhydride group (or COOH group generated from the hydrolysis of the maleic anhydride group) and the oxygen groups of the silicates. The interlayer spacing of the clay increases and the interaction of the layers should be weakened. The intercalated clays with the oligomers contact PP under a strong shear field. If the miscibility of PP-MA with PP is good enough to disperse at the molecular level, the exfoliation of the intercalated clay should take place smoothly (Figure 2.2).





**Figure 2.2** Schematic representation of the dispersion process of the organized clay in the PP matrix with the aid of PPMAs.

On the other hand, if the miscibility is not good enough, the phase separation occurs with no exfoliation. Therefore, it is quite reasonable to say not only the intercalation ability of the oligomers but also the miscibility should be a very important factor to achieve the exfoliated homogeneous dispersion of the clays in their work using PP-MA as a compatibilizer containing different amounts of maleic anhydride groups (PP-MA-1001, acid value = 26 mmol of KOH/g, PP-MA-1010, acid value = 52 mmol of KOH/g). The miscibility between PP and PP-MA-1001 is much better than that between PP and PP-MA-1010. The results are quite reasonable since the maleic anhydride is a polar group and should decrease the miscibility with PP by increasing its content in the oligomers. Therefore, the silicate clay layers in the PP-clay hybrids with PP-MA-1001 should be more exfoliated and dispersed compared to those in the PP-clay hybrids with PP-MA-1010.

Further study by the same group (Kawasumi *et al.*, 1998), found that maleic anhydride grafted PP (PP-g-MA) was able to intercalate into the inter-galleries of organomodified clay, similar to the functional oligomer, and described a facile approach for the preparation of PP/clay nanocomposite by melt intercalation using a PP-g-MA and organically modified clay. In a typical preparative method, PP/clay nanocomposite pellets were prepared by melt blending pellets of PP-g-MA and the powder of ODA-MMT at 200°C, using a twin-screw extruder. X-ray diffractometer patterns and transmission electron microscopy images showed that the silicate layers were exfoliated and uniformly dispersed in the PP-g-MA matrix.

However, PP/clay nanocomposites used PP-g-MA as compatibilizer have mechanical properties lower than the native polypropylene, due to chain scission during grafting. Therefore, the addition of PP-g-MA can result in lower mechanical properties of the final composite. Hence, there must be an optimum content of polar functional groups in order to obtain the hybrids.

Lertwimolnun and Vergnes (2005) have prepared PP/organoclay nanocomposites via direct melt intercalation in an internal mixer. Maleic anhydride grafted polypropylene (PP-g-MA) was used as a compatibilizer to improve the dispersability of the clay. The effect of concentration of PP-g-MA was investigated by varying the concentration of PP-g-MA from 0 to 40 wt% (a maleic anhydride grafted polypropylene containing 1 wt% of maleic anhydride). The organoclay used in this study (Cloisite®20A) is a Na<sup>+</sup>-montmorillonite, chemically modified with dimethyl dihydrogenated tallow quaternary ammonium chloride. The interlayer spacing of Cloisite®20A is 2.51 nm before compounding. For the uncompatibilized system, the XRD pattern exhibits no significant increase in interlayer spacing (2.56 nm after mixing). This indicates that the polypropylene does not intercalate into the interlayer, even if the montmorillonite is modified with dimethyldihydrogenated tallow ammonium ions. The interlayer spacing increases progressively, from 2.83 nm for 5 wt% compatibilizer to 3.11 nm for 15 wt% compatibilizer. However, in the range of 15–25 wt% compatibilizer, no significant increase in interlayer spacing is observed and no further improvement on the dispersibility is observed for PP-g-MA content above 25 wt%.

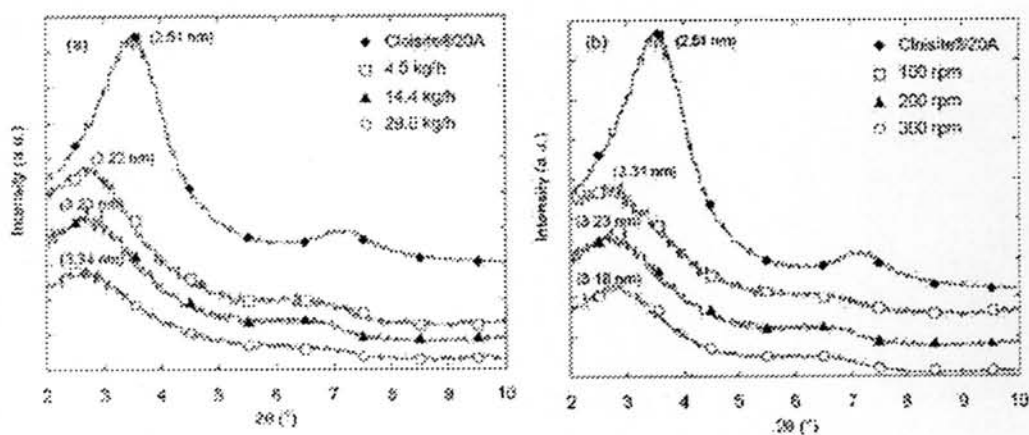
A year later, Lertwimolnun and Vergnes (2006) also studied the effect of processing conditions on the formation of PP/organoclay nanocomposites in a twin screw

extruder. All polymers used in this study were provided by Atofina. The homopolymer polypropylene (PP) of extrusion grade (PPH5060) had a MFI of 6 g/10 min and a melting temperature of 164°C. The compatibilizer (OREVAC<sup>®</sup>CA100) was a maleic anhydride (MA) functionalized PP (PP-g-MA), containing 1 wt% of MA. Its MFI and melting temperature were 10 g/10 min and 161°C, respectively. The organoclay used was Cloisite<sup>®</sup>20A purchased from Southern Clay Products (Gonzales, TX). It was a Nanomontmorillonite, chemically modified with dimethyl dehydrogenated tallow quaternary ammonium chloride.

The effects of operating conditions on the intercalation state were examined using WAXD measurements. The results were interpreted by observing the evolution of interlayer spacing. The WAXD spectra of extrudate samples and original Cloisite<sup>®</sup>20A were shown in Figure 2.3. The calculated values of  $d_{001}$  were also reported. In all cases, the peak characteristic of the {001} basal reflection of organoclay was observed. Compared with the original clay, it was shifted toward lower angles, indicating the increase in interlayer spacing after extrusion process (from 2.51 to 3.2 nm). These results showed that an intercalated structure was formed and that the organoclay still retained an ordered structure after melt compounding. In addition, the absence of the basal reflection of the original clay (at  $2\theta = 3.5^\circ$ ) indicates that a complete intercalated structure is obtained for all composites. The operating conditions seemed to have no significant influence on the state of intercalation. The maximum difference of interlayer spacing for the composites extruded at different conditions was of the same order that the one determined on different samples for the same condition ( $\pm 0.12$  nm). This variation was dependent on the diffusion time. In our study, the minimum mean residence time was around 47 sec at  $Q = 29.0$  kg/h and  $N = 200$  rpm. This showed that the short processing time in extrusion was not a limit to achieve a full intercalated structure. Furthermore, several researchers reported that the thermal decomposition of long chain aliphatic quaternary ammonium cations can occur at temperature ranges of 180–200°C, resulting in a reduction of interlayer spacing. Their results show that this effect was not significantly important in the processing conditions they studied. All the composites obtained presented an interlayer spacing higher than the original Cloisite<sup>®</sup>20A. This could be explained by the fact that



the intercalation process was rapid and allowed intercalation before eventual degradation of the quaternary ammonium.



**Figure 2.3** WAXD patterns of nanocomposite prepared with (a) different feed rates at same screw speed ( $N = 200$  rpm) and (b) different screw speeds at same feed rate ( $Q = 14.4$  kg/h).

The effects of compatibilizer characteristics and concentration on nanostructure of PP composite with organically modified clays was examined by Marchant and Jayaraman (2002), the extent of delaminating in different nanocomposites has been quantified from analysis of several TEM images for each specimen by a product of the single particle volume fraction and the intrinsic viscosity of such particles. This measure correlates directly with the ratio of the low shear complex viscosity magnitude for the molten composite to that of the silicate-free mixture. Thus, the low-frequency relative viscosity has been shown to be an effective rheological probe for distinguishing between structures with different extents of exfoliation. The molar ratio of functional groups to compatibilizer chains is a better parameter for ranking the compatibilizer effectiveness than the AN, which is a weight ratio. With higher values of the molar ratio, lower concentrations of compatibilizer are required for significant exfoliation. With the highest molar ratio compatibilizer (AN ) 15), an optimum compatibilizer concentration of about 10 wt % leads to a composite with the most exfoliated structure.

Ismail et al. (2002) studied the effect of various compatibilizers on mechanical properties of polystyrene/polypropylene blend. Blends of 20/80, 50/50 and 80/20 (wt%) were prepared through melt blending in a single screw extruder at a blend temperature of 200°C and a screw speed of 40 rpm. Four compatibilizers, viz. polystyrene-block-poly (ethylene-butylene)-block-polystyrene (SEBS), Surlyn<sup>®</sup>, ethylene vinyl acetate (EVA) and sodium salt hydrate of 4 styrenesulfonic acid (4ssa, ssh) with concentration of 7.5% w/w were used. It can be stated that those blends with 7.5% SEBS produce an improvement in toughness of PS/PP blends for all blend compositions. Moreover, the brittle behavior can be converted into a quite ductile material in 50/50 and 80/20 PS/PP blend with the addition of SEBS. The addition of 7.5% Surlyn<sup>®</sup> increased the tensile strength and Young's modulus of the blend. In the case of adding 7.5% of EVA in PS/PP blend, the results indicate that a slight improvement in elongation at break was obtained, whereas incorporation of 7.5% sodium salt hydrate of 4 styrene sulfonic acid has reduced the properties in all blend compositions.

Recently, structure-property relationships for nanocomposites formed by melt processing from a series of organoclays and poly (ethylene-co-methacrylic acid) ionomers were studied by Shah et al. (2005). The chemical structure of the alkyl ammonium surfactants was systematically varied to determine how specific groups might affect the mechanical properties and morphology of these composites. Four distinct surfactant structural effects have been identified that lead to improved levels of exfoliation and higher stiffness for these nanocomposites: (1) higher number of alkyl tails on the amine rather than one, (2) longer alkyl tails instead of shorter ones, (3) 2-hydroxy-ethyl groups as opposed to methyl groups on the ammonium ion, and (4) excess amount of the amine surfactant on the clay instead of an equivalent amount. Most of these trends are opposite to what has been observed in nylon 6 based. It seems that nylon 6 has a higher affinity for the silicate surface than does the poly(ethylene-co-methacrylic acid) ionomer while the latter is less repelled by the alkyl tails than the polyamide. Hence, surfactant structural aspects that lead to more shielding of the silicate surface or increased alkyl material leads to improved exfoliation in the ionomer. These observations are similar to those seen with LDPE and

LLDPE based nanocomposites. It should also be noted that, although some organoclays were exfoliated better than others, none of the ionomer-based nanocomposites exhibited exfoliation levels as great as those seen in nylon 6 nanocomposites. Nevertheless, nanocomposites prepared from such ionomers offer promising improvements in performance and may be particularly suitable for barrier applications.

In this work, the system was made up of three components, polypropylene, the organoclay and the indicator dye. The first, polypropylene, was selected to be the matrix due to low cost, great processibility and wide range of applications. However, it has some disadvantages such as low toughness and low service temperature. In order to improve the properties of polypropylene, the organoclay as the second component needs to be introduced to overcome these problems. For the modification of clay, DOEM exhibited the largest interlayer spacing, promising the most suitable choice for producing PP/clay nanocomposites. The nanoclay composites incorporating the indicator dye were melt compounded through a twin screw extruder using Surlyn<sup>®</sup> as a reactive compatibilizer. Subsequently, the nanoclay composites were fabricated into the sample sheet for color testing.