# MOISTURE ABSORPTION BEHAVIOR OF MALEIC ANHYDRIDE GRAFTED POLYETHYLENE MODIFIED ETHYLENE VINYL ACETATE COPOLYMER / HIGH DENSITY POLYETHYLENE NANOCOMPOSITES

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# MOISTURE ABSORPTION BEHAVIOR OF MALEIC ANHYDRIDE GRAFTED POLYETHYLENE MODIFIED ETHYLENE VINYL ACETATE COPOLYMER / HIGH DENSITY POLYETHYLENE NANOCOMPOSITES

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**Abstract-** The compatibilized poly ethylene vinyl acetate copolymer (EVA)/high density polyethylene (HDPE) /organo-modified montmorillonite (OMMT) blend nanocomposites were prepared in a co-rotating twin-screw extruder followed by injection molding. Montmorillonite clay was modified by octadecylamine and aminopropyltriethoxysilane to make it organophilic. Maleic anhydride grafted high-density polyethylene was used as a Compatibilizer. Nanoclay was added in different proportions to the selected EVA/HDPE blend composition. The concentration of nanoclay was varied from1 to 5 phr in the polymer blend. The resulting nanocomposites were evaluated in terms of their water absorption behavior. Moisture absorption behavior of compatibilized blends is lower than their corresponding blend. On adding the nanoclay the moisture absorption behavior of blend nanocomposites changed at 4 phr nanoclay loading.

*Keywords- Ethylene vinyl acetate copolymer (EVA); High density polyethylene (HDPE) ; Maleic anhydride grafted polyethylene (MA-g-PE); organophilic Montmorillonite (OMMT); Moisture absorption Property*

## I. INTRODUCTION

Ethylene vinyl acetate copolymer (EVA) and high density polyethylene (HDPE) polymers are incompatible. This incompatibility is due to the differences in the polarity and hydrophilicity of EVA and HDPE phases, which leads to poor mechanical properties. The most useful method at present is to add small amount of Compatibilizer such as maleic anhydride grafted polyolefins that are miscible with the base polyolefins [1].

Polar character of the anhydride creates affinity for the clay material in such a way that the polyolefin serves as a compatibilizer between the matrix and filler. Further, several studies have been reported on processing of polymer/clay composites using single polymer [2-3] and blends of polymers [4]. However, very little work has been done on processing of nanocomposites using polymer blend. The incompatibility and poor interfacial adhesion due to the differences in the polarity and hydrophilicity of EVA and HDPE phases lead to poor mechanical properties. These problems, however, can be solved by using a compatibilizer. MA-g-PE is used as a compatibilizer. HDPE is impermeable towards water or moisture. Since, the organoclay is hygroscopic, some absorbed moistures can be released by the organoclay to hydrolyze maleic anhydride grafts. Another chance is that the hydroxyl group (OH) in the clay and/or the hydrogen substituent of the organic modifier can change the maleic anhydride group to maleic acid groups. The use of a post-consumer polypropylene with a low percentage of

EVA leading to improved resistance to water absorption and better mechanical properties is also reported by Espert et al. [5]. In our previous paper, compatibilized Poly (ethylene-co-vinyl acetate) (EVA)/ high density polyethylene (HDPE)/ organo modified montmorillonite (OMMT) nanocomposites are prepared by melt mixing technique. Tambe et al. reported that the incorporation of nanoclay in the polymer blends does not show appreciable change in water absorption [6].

There is very limited available information on moisture absorption behavior of high EVA content EVA/HDPE/OMMT nanocomposites. This work aims to fully characterize the effects of nanoclay on the moisture absorption behavior of compatibilized EVA/HDPE/OMMT nanocomposites. In this paper, the effect of nanoclay addition on the moisture absorption behaviour of compatibilized EVA/HDPE blends is determined and analyzed .

## II. EXPERIMENTAL

### Materials
Ethylene vinyl acetate copolymer (TAISOX 7350 M ) in granular form having density 0.93 g/cm3, melt flow index 2.5 g/10min, VAc 18% and melting point 87°C was obtained from Nippon Unicar. Co. Ltd., Japan. High density polyethylene (HD 50MA 180) in granular form obtained from Reliance Industries, Hazira, Gujarat (India), had density 0.95 g/cm$^3$ and melting point 131°C. Maleic anhydride grafted

polyethylene (E-156) having density 0.92 g/cm$^3$ and MFI 1.5 g/10 min was supplied from Pluss Polymer Pvt Ltd, Faridabad. The nanoclay (Nanomer® 1.31PS), a montmorillonite modified by 15-35 wt % octadecylamine and 0.5-5 wt% aminopropyl triethoxy silane was obtained from Sigma Aldrich.

## Preparation of EVA/HDPE blends and their Nanocomposites

EVA/HDPE blends having higher loading of EVA and their nanocomposites were melt-mixed in a Berstorff co-rotating twin screw extruder (screw diameter: 25mm, L/D=48) at a constant rotating speed of 200rpm. Extrudates were cooled with water and pelletized. Table 1 showed the sequential addition of EVA, HDPE, compatibilizer and nanoclay. Test specimens were prepared by injection moulding (JSW 180H). The barrel temperature was in the range of 140-230°C and injection pressure was 80 MPa.

Table1. Sample compositions

| Sample Designator | wt % Polymer | | Compatibilizer MA-g-PE (phr) | Organoclay (phr) |
| --- | --- | --- | --- | --- |
| | EVA | HDPE | | |
| 70/30 | 70 | 30 | | - |
| 70/30/1MA | 70 | 30 | 1 | - |
| 70/30/2MA | 70 | 30 | 2 | - |
| 70/30/3MA | 70 | 30 | 3 | - |
| 70/30/4MA | 70 | 30 | 4 | - |
| 70/30/2MA/1 NC | 70 | 30 | 2 | 1 |
| 70/30/2MA/2 NC | 70 | 30 | 2 | 2 |
| 70/30/2MA/3 NC | 70 | 30 | 2 | 3 |
| 70/30/2MA/4 NC | 70 | 30 | 2 | 4 |
| 70/30/2MA/5 NC | 70 | 30 | 2 | 5 |

## Moisture Absorption Properties

In order to measure moisture absorption of EVA/HDPE nanocomposites specimens (50 mm diameter disc) were dried in a hot-air oven for 24 hours at 60$^o$C and cooled in a desiccator according to ASTM D-570. The weight of dried specimens was measured to a precission of 0.001 gram and placed in an enclosure containing distilled water. The specimens were removed and then weighed to determine the weight change or moisture uptake periodically. The specimens were immediately placed back after each measurement. For each measurement, specimens were removed from the water and the surface water was wiped off using blotting paper. The weights of the specimens were measured at every 1 day during the time immersion. The weight change of the specimens was measured at every 1 day until there was no further change, i.e., its moisture absorption reached an equilibrium. The measurements were terminated after the equilibrium weight was reached. Five specimens were measured for each sample and the results were averaged to obtain a mean value. The values of the water absorption ($W_a$) in percentage were calculated using the following formula:

$$\%W_a = W_f - W_i \times 100 \,\square\, W_i$$

Where $W_i$ is initial weight of oven-dry specimen (g), $W_f$ is weight of specimen (g) after interval of 1 day after immersion in distilled water.

## III. RESULTS & DISCUSSIONS

### Effect of Compatibilizer on EVA/HDPE System

Figure 1 shows percentage of moisture absorption as a function of square root of time for 70/30 system and its corresponding compatibilized blend samples immersed in distilled water at room temperature.
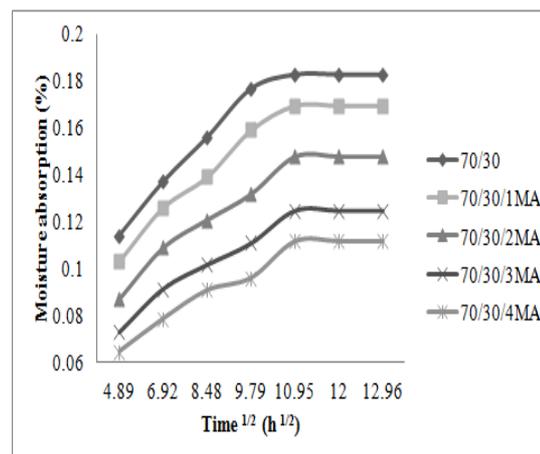


**Figure 1. Effect of different loading of compatibilizer on the moisture absorption behavior of EVA/HDPE blends.**

It can be seen from Figure 1 that the water absorption of blends decreases with increase in concentration of compatibilizer from 0 to 4phr. The maximum percentage weight gain for 70/30, 1, 2, 3 and 4 compatibilizer loaded blends specimens of immersed at room temperature for 120 hours is 0.183, 0.169, 0.147, 0.124 and 0.111 %, respectively. It is found that compatibilized blends show lower water absorption compared to its corresponding blend. The water uptake process for all specimens is linear in the beginning, then slows saturation after certain time. In case of 70/30 maximum water absorbption takes place. 70/30 system having 4 phr compatibilizer shows minimum water absorption. From figure 3, it is clear that diffusivity decreases significantly up to 2 phr compatibilizer. Beyond 2phr concentration, there are no appreciable changes in diffusivity of blends. Generally water absorption increases with immersion

time, reaching a certain value beyond which no more weight increased. Saturation of moisture uptake for all compatibilized samples reaches after 120 hours (5days).
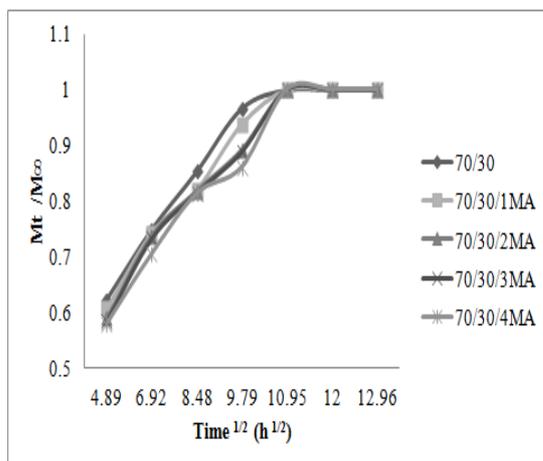


**Figure 2. Water uptake ratio ($M_t/M_\infty$) versus $t_{1/2}$ for compatibilized blend formulations.**

From figure 2, it is observed that the plot of $Mt/M\infty$ vs. $t^{1/2}$ is linear at the initial stage and the diffusivity can be calculated from its slope, hence, the diffusion behavior of water may be considered to follow the Fickian type diffusion.

**Table 2:** Diffusion parameter for EVA/HDPE system with different loading of compatibilizer and nanoclay.

| Sample Designation | $M\infty$ [%] | D [ $m^2$/s ]. $10^{-12}$ |
|---|---|---|
| 70/30 | 0.183 | 1.59 |
| 70/30/1MA | 0.169 | 1.51 |
| 70/30/2MA | 0.147 | 1.43 |
| 70/30/3MA | 0.124 | 1.4 |
| 70/30/4MA | 0.111 | 1.38 |
| 70/30/2MA/1NC | 0.127 | 1.27 |
| 70/30/2MA/2NC | 0.104 | 1.14 |
| 70/30/2MA/3NC | 0.076 | 0.96 |
| 70/30/2MA/4NC | 0.059 | 0.80 |
| 70/30/2MA/5NC | 0.053 | 0.76 |

Table 2 summarizes the diffusion coefficient at room temperature. The diffusion coefficients $D$ can be used to compare the diffusion rate in the uncompatibilized blend to the compatibilized one, and to estimate how much time total moisture saturation of a sample takes. It is observed from the table 2 of the diffusion coefficient that the diffusion coefficient decreases as the amount of compatibilizer increases as shown in figure 3.
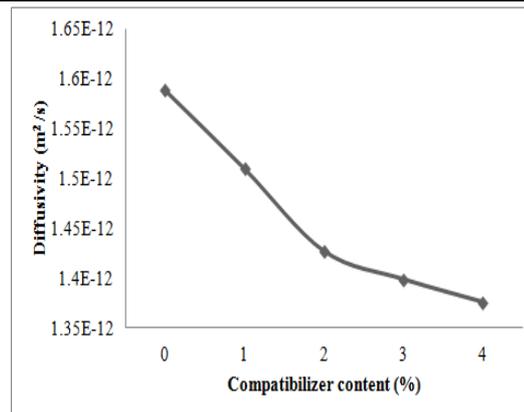


**Figure 3. Diffusion coefficient of compatibilized blends as function of compatibilizer content.**

From figure 3, it is clear that diffusivity decreases significantly up to 2 phr compatibilizer. Beyond 2phr concentration there is no appreciable changes in diffusivity of blends. Therefore, 70/30/2MA is selected for further study.

The purpose of compatibilizer is to improve the interfacial bonding between immiscible blends. Figure 1 shows clearly the effect of compatibilizer on the water absorption characteristics of EVA/ HDPE (70/30) blends. It can be seen that the MA-g-PE and EVA/HDPE blends exhibits decreased rate of water absorption compared to unmodified polymer blend. The compatibilizer builds up chemical bonds, which reduce the moisture-caused EVA/HDPE debonding. It is found that compatibilizer, MA-g-PE has the hydrophobic segment and the hydroxyl segment, which will result in strong physical interaction between HDPE and EVA on the interface. This in turn reduces the extent of water absorption. A strong adhesion at the interface is needed for an effective transfer of stress and load distribution throughout the interface.

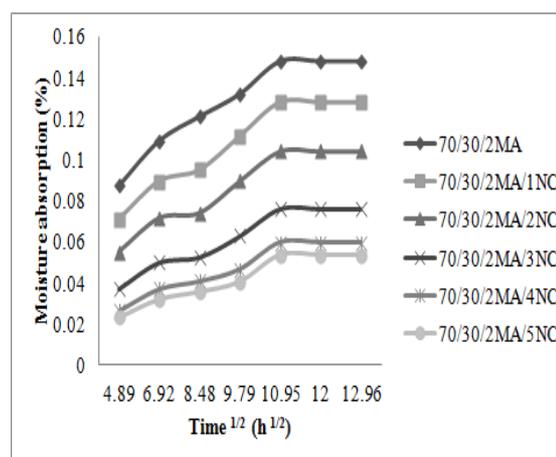**Effect of Nanoclay on compatibilized EVA/HDPE System**



**Figure 4. Effect of different loading of nanoclay on the moisture absorption behavior of compatibilized EVA/HDPE blends.**

Figure 4 shows percentage of moisture absorption as a function of square root of time for 70/30/2MA system and its corresponding nanocomposites samples immersed in distilled water at room temperature. It can be seen from Figure 4 that the water absorption of composites decreases with increase in concentration of nanoclay from 0 to 5phr. The maximum percentage weight gain for 70/30/2MA, 1,2, 3, 4 and 5 nanoclay loaded nanocomposites specimens of immersed at room temperature for 120 h is 0.147, 0.127, 0.104, 0.076, 0.059 and 0.053 %, respectively. It is found that nanocomposites show lower water absorption compared to its corresponding blend. The water uptake process for all specimens is linear in the beginning, then slows saturation after certain time. In case of 70/30/2MA maximum water absorption takes place. 70/30/2MA blend having 5phr nano clay shows minimum water absorpption. From figure 6, it is clear that diffusivity decreases significantly up to 4 phr nanoclay. Beyond 4phr concentration there is no appreciable changes in diffusivity of blends. Generally water absorption increases with immersion time, reaching a certain value beyond which no more weight increased. Saturation of moisture uptake for all nanocomposites samples reaches after 120 hours.

Moisture absorption is generally considered to be independent of moisture concentration, the diffusion of moisture is generally considered to obey Fick's law [7]. The solution for Fick's law short times for the initial stage of diffusion:

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2}$$

(1)

where $M_t$ is the mass gain at reduced time and $M_\infty$ is the maximum mass gain at the equilibrium state and $l$ is half the thickness of the polymer sample.
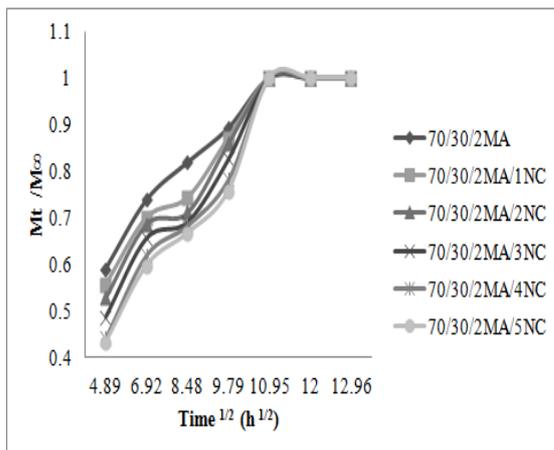


**Figure 5. Water uptake ratio ($M_t/M_\infty$) versus $t_{1/2}$ for nanocomposite formulations.**

From figure 5, it is observed that the plot of $M_t/M_\infty$ vs. $t^{1/2}$ is linear at the initial stage and the diffusivity can be calculated from its slope, hence, the diffusion

behavior of water may be considered to follow the Fickian type diffusion. In the initial stage of the absorption, up to approximately $M_t/M_\infty = 0.5$ the increase in mass shows a linear relationship with the square root of time [8,9]. Diffusion coefficient could be determined from the slope of the normalized weight change using Equation 1.

Table 2 summarizes the diffusion coefficient at room temperature. The diffusion coefficients $D$ can be used to compare the diffusion rate in the unfilled blend to the nanocomposites one, and to estimate how much time total moisture saturation of a sample takes. It is observed from the table 2 of the diffusion coefficient that the diffusion coefficient decreases as the amount of nanoclay increases as shown in figure 6.
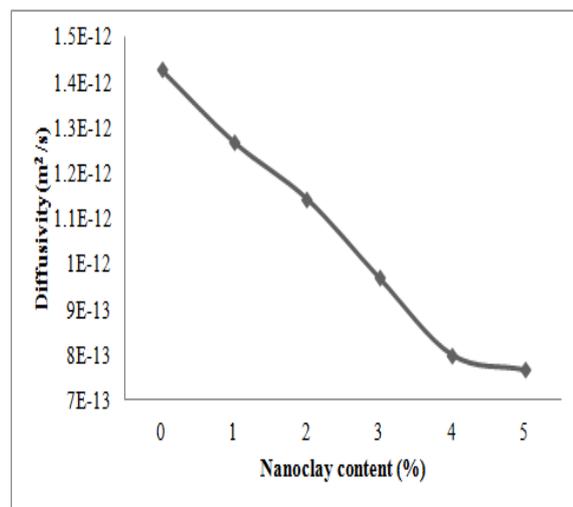


**Figure 6. Diffusion coefficient of nanocomposites as function of organoclay content.**

From figure 6, it is clear that diffusivity decreases significantly up to 4phr nanoclay. Beyond 4phr concentration there is constant diffusivity for nanocomposite.

Both the initial rate of water absorption and the maximum water uptake decrease for all nanocomposites samples as the nanoclay concentration increases. This phenomenon can be explained by considering the hydrophobic nature of organomodified nanoclay. In general, layered silicate is modified with octadecylamine and aminopropyl triethoxy silane to facilitate its interaction with the polymer, because octadecylamine and aminopropyl triethoxy silane makes the hydrophilic silicate surface organophilic. The rate of water absorption in EVA/HDPE nanocomposites is found to be less as compared to the unfilled blend because of the impermeable nature of silicate layers in the polymer. These layers increase the path-length for diffusion through the polymer. The increase in the path length gives increased barrier properties for nanocomposites. Similar type of moisture absorption is also observed earlier for nylon 6/ clay hybrids (10).

Both the initial rate of water absorption and the maximum water uptake decrease for all nanocomposites samples as the nanoclay concentration increases. This phenomenon can be explained by considering the hydrophobic nature of organomodified nanoclay. In general, layered silicate is modified with octadecylamine and aminopropyl triethoxy silane to facilitate its interaction with the polymer, because octadecylamine and aminopropyl triethoxy silane makes the hydrophilic silicate surface organophilic. The dispersion of hydrophilic silicate layers in EVA/HDPE system can be achieved by using MA-g-PE compatibilizer.

It can be seen from Figure 4, the samples absorb water with immersion time until a constant weight is obtained. It is believed that the tortuous path made by the dispersed nanoparticles acts as a barrier for the water diffusion inside the speimens [11]. The nanoparticles also limit mobility of the polymer chains and decrease diffusion of water molecules into the samples. If water molecule wants to permeate the samples, it has to pass through these channels which reduce the diffusion rate of water molecule in the sample [12]. Also, conversion of the nanoclay surface particles from hydrophilic to hydrophobic owing to alkylammonium ion exchange decreases water absorption of the samples [11]. Reduction in water absorption due to presence of montmorillonite in the polymer blends has also been reported by other workers [11, 13]. Because of the presence of silanol groups on the edges of the silicate layers, and the swelling ability of the OMMT clays in water, the water absorption of the samples still exist [14]. It is found that MA-g-PE not only enhances the compatibility of HDPE with EVA but also improves adhesion of the particles of nanoclay and EVA/HDPE blend. Therefore, it can be concluded that the organoclay can have its maximum compatibilizing effect, only in the presence of the MA-g-PE compatibilizer.

## IV. CONCLUSION

- Water absorption of the nanocomposites increases with immersion time, reaching a certain value at saturation point and the composites water content remain constant.
- with increase of the MA-g-PE content, water absorption decreases. Above 2phr MA-g-PE decrement in water absorption is not significant in EVA/HDPE system. Similarly above 4phr nanoclay concentration decrement in water absorption is constant in compatibilized EVA/HDPE system.

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