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Research Paper

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Studies on the Mechanical and Water uptake Properties of Some Polyolefins / Corn Starch Blends (1)

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Abstract: - Corn starch blends of high density- and low density polyethylene have been prepared by injection moulding technique. Maleic anhydrides- graft-polyethylene was used as a compatibilizers. The effect of corn starch content on the blends was evaluated by mechanical property measurements and water uptake tests. Results indicated that the tensile strength of the blends decreased with increase in corn starch contents. While the elongation at break of low density polyethylene-corn starch blends decreased with increase in starch content, the elongation at break of high density polyethylene/corn starch blends first decreased with increase in starch content, up to 7.25 wt %, and there-after, decreased with further increase in corn starch contents. The addition of maleic anhydride-graft-polyethylene was found to improve the tensile strength and elongation at break of which increase in corn starch content, and immersion period; and tended to level off after the fourth day of immersion in water. The amount of water absorbed by the blends was appreciably decreased on incorporation of maleic anhydride-graft-polyethylene into the blends.

Keywords: - polyethylene, corn starch, maleic anhydride–graft–polyethylene, blends, mechanical properties * Correspondence to ; Isaac O . Igwe

I. INTRODUCTION

Starch is a natural polymer which is referred to as a polysaccharide. It is produced by all green plants, and consists of two distinct molecules, the amylose (linear polymer), and amylopectin(branched- polymer) [1]. Starch from various botanical sources are among the most abundant, renewable and inexpensive natural biopolymers. Using starch to partially replace synthetic plastics will not only reduce the dependence on petroleum-based plastics, but also reduce plastic wastes. It is common knowledge, however, that biodegradable plastics from starch cannot compete with conventional petroleum-based plastics because of their poor mechanical properties [2]. Most recently, starch has received maximum attention in the preparation of biodegradable plastics, especially for one time use plastics, because it is the most abundant, degradable, low cost natural polymer. It is equally available throughout the year. Partial substitution of synthetic plastics with materials like starch provides not only cheap filler but also biodegradation properties to the final products [3]. Thus, the addition of starch to synthetic plastics like polypropylene [4], poly (vinyl alcohol) [5], high density polyethylene [6,7], and linear low density polyethylene [8,9], has been reported to enhance their biodegradability. In blends of starch with synthetic polymers such as polystyrene, and polypropylene, the hydrophilic nature of starch leads to poor adhesion (miscibility) with the synthetic polymers, which are hydrophobic in nature. To improve their compatibility, various attempts had been made to modify either starch or the synthetic polymer, [10]. It has been found that plasticisers, coupling agents, or modified starch only partially improved the dispersion of starch in the synthetic polymer such as polyethylene, and their interfacial properties because of their limited interaction,[11,12]. Another approach was to use poly(ethylene-co-acrylic), poly(ethylene-co-vinylalcohol) or oxidized polyethylene ascompatibilizer in polyethylene-starch composites, but the composites had unsatisfactory mechanical properties, [13, 14]. Another method to improve the miscibility of phases in starch- polyethylene blends is the chemical modification of the hydroxyl groups of the starch to induce hydrophilicity into it. Octenyl succinate starch metal ion complexes were combined with polyethylene to create a biodegradable plastic with good tensile strength[15]. As part of our effort to investigate the biodegradation of high and low density polyethylene/corn starch blends, we report here, the effect of maleic

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anhydride-graft-polyethylene as a compatibilizer on some properties of high- and low density polyethylene / corn starch blends.

2.1 Materials

II. MATERIALS AND METHODS

The high- and low density polyethylene used in this study were obtained from Ceeplast Industries, Aba, Nigeria. The density of the polymers are 0.97, and 0.952 g /cm³ respectively. They have melt flow indexes of 9.0 g/10 mins, at 230 $^{\circ}$ C and 2.0 g/10mins at 190 $^{\circ}$ C respectively. The corn starch was obtained from the Crop Science Department, Anambra State University, Uli, Nigeria. The starch was dried at 120 $^{\circ}$ C for 24 hrs, to a moisture content of < 1.5 % prior to sample preparation. The maleic anhydride-graft-polyethylene (MA-g-PE) was purchased from FINLAB Chemicals, Owerri, Nigeria. It is a product of Sigma Aldrich, USA and it's viscosity is between 1,700.00 to 4,500 cps at 140 $^{\circ}$ C.

2.2 Sample Preparation

The high-, and low density polyethylene blends of corn starch were prepared by thoroughly mixing the weighed amounts of the polymer with appropriate corn starch quantities (0, 2.5, 5.0, 7.25, 10.0, 12.50, and 15.0 wt %). The high-, or low density polyethylene was melted and homogenized with the corn starch in an injection moulding machine .The blends were extruded as sheets. Similarly, high-, or low density polyethylene blends in the presence of the compatibilizer, maleic anhydride-g-polyethylene (MA-g-PE) were prepared as described above. The compatibilizer level was 10.00 wt % based on the weight of corn starch in the blend.

2.3 Testing on the Blends

The tensile properties of the dumbbell-shaped samples of the blends were measured according to the ASTM D 638 specification. The elongation at break(EB) was also recorded along the meter rule pointer at 200 - 100 mm. The Rockwell hardness (ASTM D 785), and specific gravity (ASTM D 792) properties of the blends were determined using standard methods.

2.4 Water Uptake

The blends specimens were dried at 85 0 C in an oven until a constant weight was attained prior to immersion. The water uptake tests were performed to last for a period of six weeks. Weight gains were recorded by periodic removal of the specimens from the water. Water adhering on the surface of the specimens were carefully removed with filter paper before weighing on a balance with a precision of 1 mg . The percentage of water uptake at different times (W_t) was calculated according to the equation:

 W_{t} (%) = $W_{2} W_{1} / W_{1} x 100$

where W_1 and W_2 are the weights of the dried sample and the samples after immersion time, t.

III. RESULTS AND DISCUSSSIONS

(1)

The tensile properties of high density polyethylene and low density polyethylene/corn starch blends with and without maleic anhydride-graft-polyethylene are shown in **Figure 1**. When the corn starch content increased, the tensile strength of the blends decreased, presumably because of incompatibility of the polyolefins and corn starch. It is probable that the inclusion of corn starch in the polyolefin matrices caused a very significant stress concentration. In effect, fracture could be initiated from the weak interface of the blends, due to their envisaged poor interfacial adhesion, thus resulting in reduced tensile properties. *Thakore et al [3]*, who investigated low density polyethylene/potato starch or starch acetate blends found that the tensile strength of the blends decreased with increased starch or starch acetate content. The higher tensile strength of high density polyethylene as compared to low density polyethylene is attributed to the former's higher density, lack of branching, and stronger intermolecular force of attraction that exists in its chains according to *Karyn [16]*. Similarly, *Lin et al [2]* who investigated low density polyethylene/corn starch blends found results in similar to ours.



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Figure 1: Plot of tensile strength versus corn starch content for compatibilized and uncompatibilized HDPE, and LDPE Corn Starch Blends.

The plots show that the tensile strength of high density polyethylene/ corn starch blends were in all cases higher than those of low density polyethylene/starch blends, with the determined tensile strength of high density polyethylene(21.98 Nm⁻²) being higher than that of low density polyethylene (12.17 Nm⁻²). When the compatibilizer (MA-g-PE) was added to the polyolefin blends, the tensile properties of the blends were increased and two types of behaviours can be observed;

(i) the tensile strength of the high density polyethylene/corn starch blends were greatly increased at maleic anhydride-graft-polyethylene contents, 4.0 wt % based on 10 % corn starch content, and thereafter, decreased after MA-g-PE content, 4.0 wt.%. The decrease in the tensile strength of compatibilized high density polyethylene, after the addition of 4.0 wt % maleic anhydride-graft-polyethylene is probably due to the molecular morphology of HDPE near the surface or in the bulk of the plastic phase *Sanadi et al, [19]*. Transcrystallization and changes in the apparent strength of the bulk matrix can result to changes in the contribution of the matrix to the composites strength

(ii) the tensile strength of the low density polyethylene / corn starch content were gradually increased, were in all cases were smaller than that of the unblended LDPE within the MA-g-PE content investigated. It is believed that MA-g-PE increased the adhesion between the polyolefin matrices and the corn starch filler. The improved interfacial adhesion between the polyolefins and corn starch has a positive impact on the stress transfer, thus reducing the chance of interfacial debonding, and leading to improved tensile strength properties. The above results further support the assumption that the interaction between starch and MA-g-PE was a chemical one between the hydroxyl groups in corn starch and anhydride groups in MA-g-PE, because, a polar interaction between them would not improve their properties to any significant extent. In contrast to our results, *Matzinos et al [17]* who characterized LDPE/starch blends, reported an increase in the strength of the blends with starch contents of up to 50 wt % starch after which the tensile strength of the blends decreased with any further increased in starch content.





The two polyolefin blends of corn starch were observed to behave differently with increasing starch content: (i) when corn starch content was increased, the elongation at break of LDPE/corn starch blends decreased, presumably because of the heterogeneous dispersion of starch in LDPE matrix, and the incompatibility of LDPE and starch. A similar behaviour was also observed with LLDPE /starch films *Evangelista et al [10]. Thakore et al [3]*, had also reported a decrease in elongation at break of LDPE /potato starch blends with increase in potato starch content. In synthetic polymer blends, the addition of the immiscible component to a ductile matrix generally decreases the elongation properties considerably at break point *Paul, et al [18].*

(ii) the elongation at break for HDPE/corn starch blends was observed to increase with increase in starch content, up to 7.25 wt % of starch, and thereafter, decreased with further increase in corn starch content. Similar behaviour was also noticed in the variation of tensile strength of HDPE / corn starch blends with corn starch content.

(i) the elongation at break of HDPE /corn starch blends increased with increase in MA-g-PE content, up to 30 wt % and thereafter, decreased with any further increase in the MA-g-PE content. However, the resulting decrease in elongation at break values are greater when compared to the uncompatibilized blends.

(ii) between 1.0 wt % and 2.0 wt % of MA-g-PE content, the elongation at break increased, after which it decreased with further increase in MA-g-PE content.

Thakore et al [3] in their studies found that the elongation at break of LDPE/starch acetate and LDPE/starch blends increased with increase in starch acetate, and starch contents, in the blends reached a maximum, and thereafter decreased. This increase in elongation at break was attributed to the improved plasticity of starch acetate.





Figure 4: Plot of water uptake and immersion time for compatibilized and uncompatibilized LDPE /corn starch blends.

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The water uptake for uncompatibilized and compatibilized polyolefin blends are illustrated in Figures **3** and **4** respectively. The figures show progressive increase in the amount of water absorbed by HDPE-, and LDPE/starch blends with increase in the amount of starch incorporated into the polyolefins, and period of water absorption. For most of the blends, the amount of water absorbed tended to level off (i.e. equilibrium absorption) after the fourth day of immersion in water. The negligible amount of water absorbed by HDPE, and LDPE tended to remain fairly constant throughout the duration of the experiment. These polyolefins are hydrophobic. The water uptake in the blends are due to the presence of hydrophilic starch particles in the blends. Starch particles possess an abundant of hydroxyl groups in their molecules and which are available for interactions with water molecules. Thus, water molecules can saturate the surface of the polyolefin/corn starch blends easily and penetrate into the composites through voids which result in higher water uptake in a short immersion period as reported by *Sanadi, et al, and Danjija et al, [20, 21]*.

Figures 3 and 4 show that the compatibilized polyolefin blends absorbed less water when compared to the uncompatibilized blends. Thus, at each corn starch content in the blend considered, the compatibilized polyolefin blends absorbed less water when compared to the uncompatibilized blends. This is attributed to the improved adhesion obtained between the corn starch and polyolefins in the presence of MA-g- PE which reduces the water penetration into the blends.

The water absorbed by LDPE /corn starch blends is observed to be higher than those absorbed by HDPE/corn starch blends. LDPE has a high degree of short chain branching in its molecule *Katchy*, [22], and which has the capacity to loosen up the main chain structure thereby allowing the water molecules to penetrate more easily. This fact **may** account in parts for the observed high amount of water absorbed by LDPE, and its blends when compared to HDPE and its blends.

IV. CONCLUSION

Corn starch has been used to prepare blends of high density polyethylene, and low density polyethylene. When the starch content increased, the tensile strength of the blends decreased. The elongation at break(EB) of the blends was found to behave differently with increase in starch content. For LDPE, the EB of the blends decreased with increase in starch content, while for HDPE, the EB of the blends first increased with increase in starch content, up to 7.25 wt %, and thereafter, decreased with any further increase in starch content.

HDPE-, LDPE/corn starch are two- medium blend, therefore, MA-g-PE was used to improve the adhesion between the polyolefins and corn starch. The tensile strength and elongation at break of the blends were therefore improved with the addition of MA-g-PE as compatibilizer. The water uptake for both the uncompatibilized and compatibilized blends increased with the increase in corn starch content. However, the quantity of water absorbed by the compatibilized blends was in all cases lower than the uncompatibilized blends.

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