

Biocomposites from Polypropylene and Corn Cob: Effect Maleic Anhydride Polypropylene

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Abstract. The rising concern toward environmental issue, the need for more versatile polymer based materials has led to increasing interest about polymer biocomposites filled with natural organic filler from renewable and biodegradable. Biocomposites from polypropylene (PP) and corn cob (CC) were investigated. The effect corn cob content and maleic anhydride polypropylene (MAPP) as compatibilizer were studied. Results showed that addition corn cob (CC) in PP have decreased the tensile strength and elongation at break, whereas modulus of elasticity of biocomposites increased. The biocomposites with the MAPP as compatibilizer exhibited higher tensile strength and modulus of elasticity compared biocomposites without MAPP. The morphology study of biocomposites indicates that enhanced the interfacial interaction and adhesion between filler and matrix with the presence of MAPP.

Keywords: Polypropylene, corn cob, compatibilizer, biocomposites.

1. Introduction

Presently, natural fiber or lignocellulosic fiber reinforced polymeric composites are basically finding application in many fields due to the numerous advantages of using these lignocellulosic fibers as the reinforcing fillers in polymer compared to the synthetic ones. Some of the advantages are such as natural in origin (Salmah 2013; Yeng 2013a; Faisal 2013), relative cheapness, ability to recycle with production requiring little energy and ability to compete well in terms of strength per weight of material. Apart from that, it is also due to their economical production with few requirements for the equipment, low density and low specific weight which results in a higher specific strength and stiffness when compared to glass reinforced composites (John 2008).

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However, there are some drawbacks too, such as low microbial resistance and high moisture absorption of the natural fibers that can result in swelling of the fibers which arouses concern on the dimension stability of the agro or natural fiber composites. Other than that, the main drawback of the use of natural fiber as fillers is the lower processing temperature permissible due to the possibility of fiber degradation and/or the possibility of volatile emissions that could affect the composite properties (Panthapulakkal 2007). Agro-residue or field crop such as the cereal straw, flax straw, rice husk, bagasse, cornstalk, wheat straw and corncob which categorized as natural fibers are recently being considered as an alternative for the wood-plastic composites which are at present dominating the natural fiber-composite market (Kumari 2007).

The addition of the fillers to polypropylene would generally have some positive effect on its mechanical properties but even such, some drawbacks are also bound to be as most fillers and reinforcements are polar and polypropylene being a non-polar, it will result in poor adhesion between the filler and the polymer. This incompatibility will lead to poor dispersion and insufficient reinforcement with accompanying poor mechanical properties. Thus, a solution to solve this problem would be incorporating a compatibilizer (Yang 2007), addition of silane coupling agent (Ferrer 2005), chemical modification on natural filler (Tserki 2006; Aziz 2005; Acha 2003; Yeng 2013b), grafting polymer matrix with hydrophilic functional group (Wu 2005) and plasma treatment on surface of natural filler (Yuan 2004) to the reinforced polymeric composite. These methods will provide enhancement in interfacial adhesion between the filler and polymer matrix (Kim 2007).

Corn, also known as *Zea Mays* is widely cultivated around the world. Thus, corn cob is abundant and being a waste of corn industry. Moreover, the chemical compositions of corn cob containing 41.27% of cellulose, 46 % of hemicellulose, 7.4 % of lignin and 5.33 % of other organic compound. Incorporation of corn cob in polymer could have economic advantages and low environment impact. In our previous studies, the corn cob was used as filler in chitosan biocomposite film (Yeng 2013a; Yeng 2013b; Yeng 2013c).

The main disadvantage of using composites is low compatibility between hydrophilic character of the polar filler and hydrophobic character of non-polar matrix polymer (Yang 2007). Natural filler do not well disperse easily in thermoplastic polymer polyolefin and biodegradable polymer such as polyolefin and biodegradable polymer. Due to strong intermolecular hydrogen bonding between natural filler, they tend to agglomerate during compounding processing with the matrix polymer. The low compatibility and interfacial adhesion of bio composites lead to low mechanical properties of final product (Wu 2005; Aziz 2005; Acha 2003). Therefore study of ways to improve the interfacial adhesion between natural filler and matrix polymer is very important for the application of composites in industrial application. In recent years, the various methods that have been studied to improve the interfacial adhesion of composites, by modifying the natural filler surface, have included the use of maleic anhydride-grafted polypropylene (MAPP) (Yang 2007). The utilization of

maleic anhydride polypropylene (MAPP) (Fig. 1.1) provides a very effective compatibilizer for bio-composites in order to improve the natural filler-matrix interfacial interaction. In our previous studies, we have been reported the use of compatibilizer in composites to improve the properties (Chun 2013a; Chun 2013b). Park et al. (2006) reported MAPP can promote better interfacial interaction through the formation of covalent bonds between the filler and matrix.

The aim of this research to study the effect of corn cob content and maleic anhydride polypropylene (MAPP) as a compatibilizer on tensile properties and morphology of Polypropylene (PP)/Corn cob (CC) bio composites.

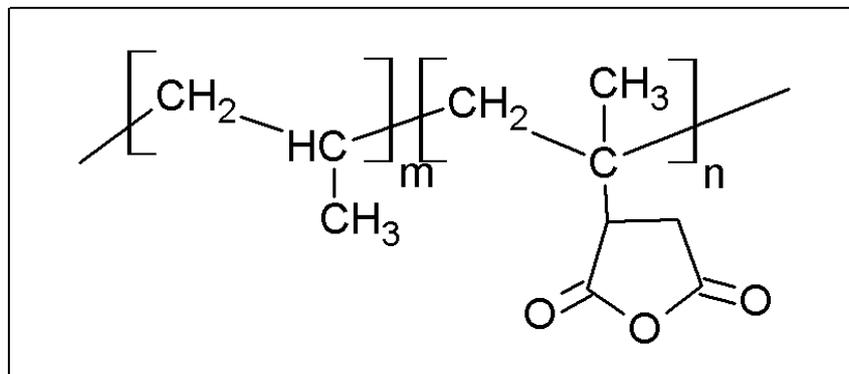


Fig. 1.1 Chemical structure of MAPP.

2. Methodology

2.1 Materials

Polypropylene grade S12232 G112 in pellet form supplied by the Polypropylene Malaysia Sdn. Bhd. The density value of PP was 0.90 g/cm³ and MFI 45 g/10 min (230°C/2.16kg, ASTM D1238). The corn cob filler used was in powder form. The fresh cobs were used in this research which was obtained from local farmer in Perlis, Malaysia. The cobs were then cleaned by peeling off the husk and the kernels. Then the corn cob was washed, chopped to slightly smaller portion followed by breaking into smaller piece. The corn cobs were dried at 80°C for 24 hours. The dried corn cob was then grounded to make finer corn cob powder. The average particle size of corn cob 66 μm, was analyzed by using the Malvern particle size analyzer equipment. The maleic anhydride polypropylene was obtained from Aldrich, Malaysia with density 0.934 g/cm³ and MFI is 115 g/10min (190°C/2.16kg, ASTM D1238).

2.2 Preparation of biocomposites

The biocomposites were prepared by using a Z-Blade mixer at temperature 180°C with rotor speed 50 rpm for 15 minutes. First polypropylene was mixed for 7 minutes until it

completely melts. The corn cob powder was added and the mixing was continuous until 8 minutes to obtain a uniform compounding of the corn cob powder in the polypropylene. For compatibilized biocomposites, the MAPP was mixed together with polypropylene. The total mixing time was 15 minutes. The biocomposites was compressed into tensile bar by using compression molding machine model GT 7014A. Tensile bar was reference to ASTM D638 tensile bar type IV with 1mm thickness. The compression procedure involved preheating at 180°C for 6 minute follow by compressing for 4 minute and subsequent cooling under pressure for 4 minutes. The formulation for the corn cob filled polypropylene composites for uncompatibilized and compatibilized biocomposites is shown in Table 2.1.

Table 2.1: Formulation of uncompatibilized and compatibilized PP/corn cob biocomposites.

Materials	Uncompatibilized biocomposites	Compatibilized biocomposites
Polypropylene (php)	100	100
Corn cob (php)	0, 10, 20, 30, 40	0, 10, 20, 30, 40
MAPP (php)	-	3*

*3 php from weight of polypropylene

2.3 Tensile properties

The tensile testing was carried out using Instron 5569 machine based on ASTM D638. The speed was set to 50 mm/min and the gauge length set to 50 mm. The tensile strength, elongation at break and modulus of elasticity for each samples were automatically calculated by the instrument software.

2.4 Morphology study

The tensile fracture surface of bio composites was studied by using Scanning Electron Microscope (SEM) machine model JOEL JSM-6460LA. This test was carried out to investigate the corn cob filler distribution and interfacial interaction between filler and matrix. The fracture ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of paladium to avoid electrostatic changing during examination.

3. Results and discussion

3.1 Tensile properties

Fig. 3.1 shows the effect of filler loading on the tensile strength of the uncompatibilized and compatibilized of PP/corn cob biocomposites. It can be seen that the tensile strength of uncompatibilized and compatibilized biocomposites decreases with increasing corn cob loading. As the filler loading increase, the poor wetting of the corn cob by the thermoplastic

matrix gave rise to poor interfacial adhesion between the filler and polypropylene matrix. At similar filler loading, the compatibilized PP/corn cob bicomposites exhibit higher tensile strength than uncompatibilized bicomposites. The higher tensile strength of compatibilized bicomposites due to the presence of MAPP, where the anhydride groups present in the MAPP covalently bonds to the hydroxyl group of the filler surface. This improved interaction and adhesion between the filler and the matrix leads to a better matrix to filler stress transfer thus producing the higher tensile strength. Fig. 3.2 displays the proposed schematic reaction between PP/corn cob bicomposite and MAPP.

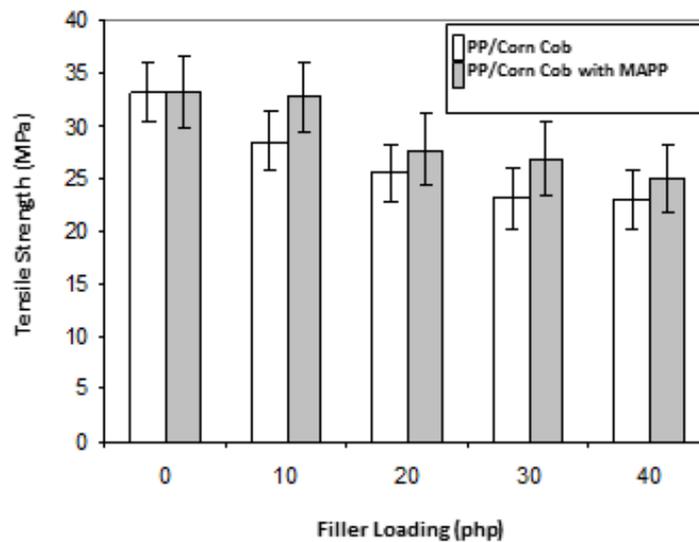


Fig 3.1 The effect of filler loading on the tensile strength of uncompatibilized and compatibilized PP/CC bicomposites.

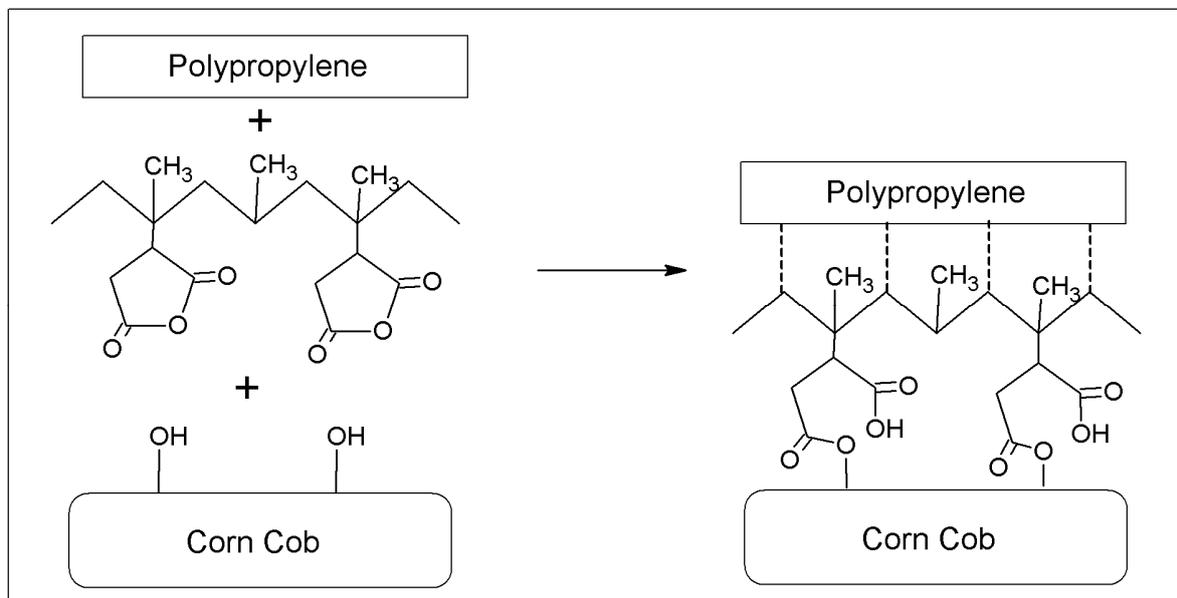


Fig 3.2 Proposed schematic reaction between PP/corn cob biocomposite and MAPP.

Fig. 3.3 illustrate the elongation at break of uncompatibilized and compatibilized PP/CC biocomposites. The elongation at break of uncompatibilized biocomposites decreased trend with CC loading increased. This due to more weak interfacial region between filler and matrix are formed. At similar filler loading, elongation at break of compatibilized PP/CC biocomposites lower than uncompatibilized biocomposites. This due to the addition of MAPP to the composites decreased the elongation at break as a result of improved adhesion between the corn cob and the polypropylene matrix thus restricting polymer mobility. It is also possible that the increase in stiffness upon addition of MAPP made the biocomposites more brittle.

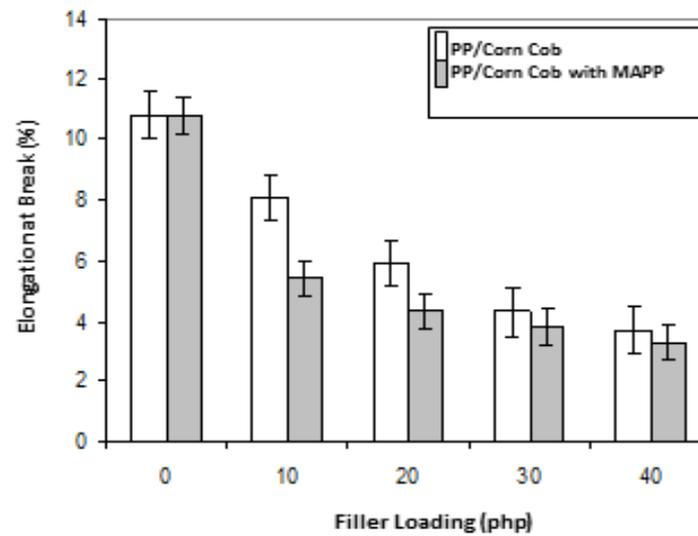


Fig. 3.3 The effect of filler loading on elongation at break of uncompatibilized compatibilized PP/CC biocomposites.

The effect of filler loading on modulus of elasticity of the uncompatibilized and compatibilized PP/CC biocomposites is illustrated in Fig 3.4. It can be seen that the modulus of elasticity increased with increasing corn cob loading. Usually an increase in the modulus of elasticity indicates that the stiffness of the biocomposite samples. However, at similar corn cob loading, the compatibilized PP/CC biocomposites exhibit slightly higher modulus of elasticity than the uncompatibilized biocomposites. This is due to the presence of MAPP which enhanced stress transfer of the filler matrix interphase as the MAPP also improves filler dispersion in the polymer matrix.

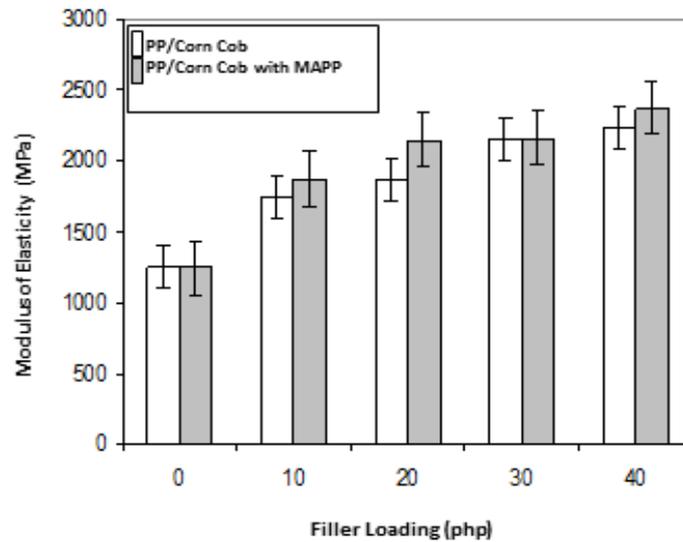


Fig. 3.4 The effect of filler loading on modulus of elasticity of uncompatibilized and compatibilized PP/CC biocomposites.

3.2 Morphology study

The tensile fractured surfaces of both uncompatibilized and compatibilized PP/CC biocomposites at 20 and 40 php are shown in Figs 3.5 to 3.8. Fig 3.5 shows the fracture surface of PP/CC composites at 20 php filler loading. It can be seen that the surface of the fracture looks rough with presence of some holes/pores and a gap between the corn cob and matrix as an effect of filler pull-out. This is due to the weak interfacial adhesion of the polar cornstalk filler and non-polar polypropylene matrix. Fig 3.6 exhibits that at higher CC loading which is 40 php, the biocomposite appears to have worse filler distribution and agglomeration which is a clear indication of weak interfacial adhesion and incompatibility between the corn cob filler and polypropylene matrix. However, by incorporating the polypropylene graft maleic anhydride (MAPP) as compatibilizer, the composites in Figs 3.7 and 3.8 showed good filler dispersion in the matrix, effective wetting of fillers by the matrix as well as strong interfacial adhesion between the components as there is less of filler particle agglomeration or pull out of filler from matrix. These observations are consistent that the MAPP compatibilizer is covalently bond to both the PP matrix and the corn cob filler to provide a more effective filler-matrix adhesion thus proving with tensile properties as discuss previously.

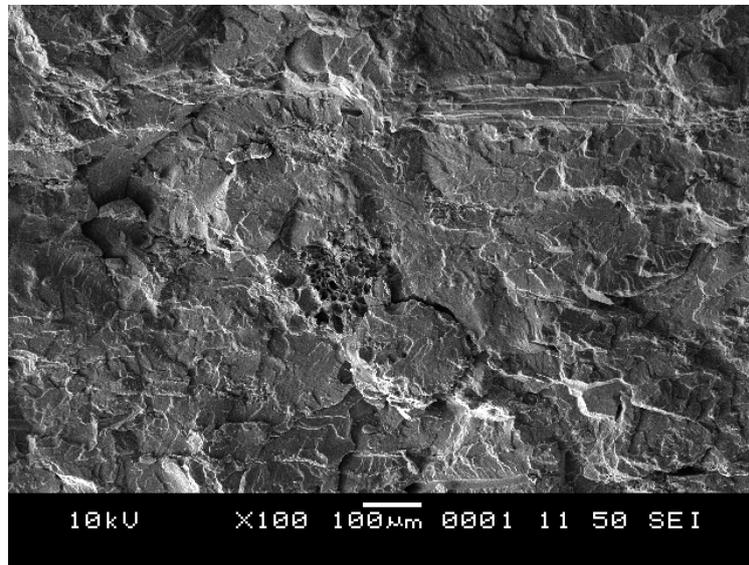


Fig. 3.5 The SEM micrograph of tensile fracture surface of uncompatibilized biocomposite (20 phr corn cob).

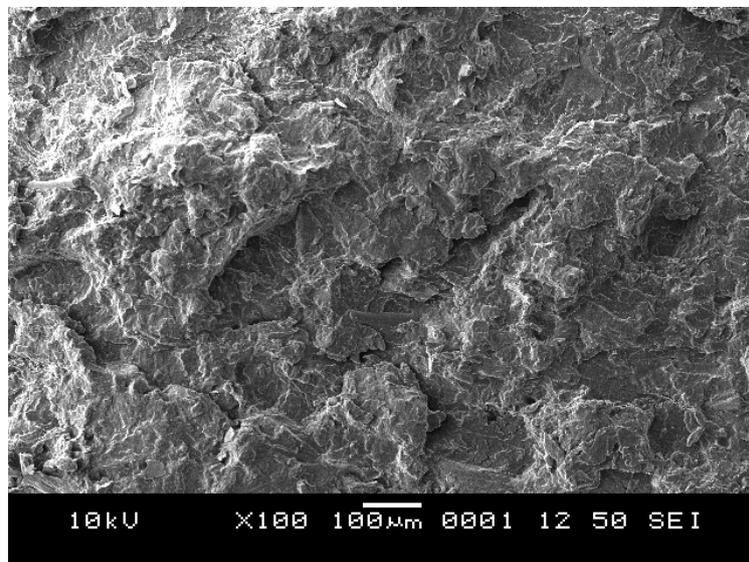


Fig. 3.6 The SEM micrograph of tensile fracture surface of uncompatibilized biocomposite (40 phr corn cob).

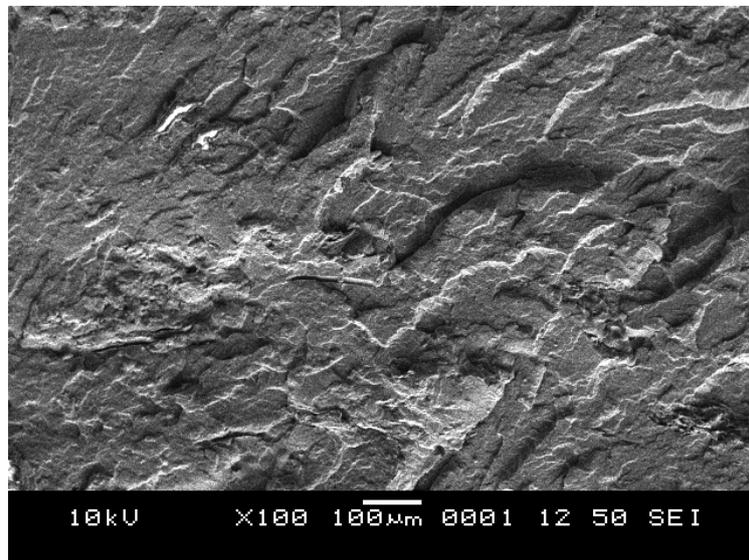


Fig. 3.7 The SEM micrograph of tensile fracture surface of compatibilized biocomposite (20 php corn cob).

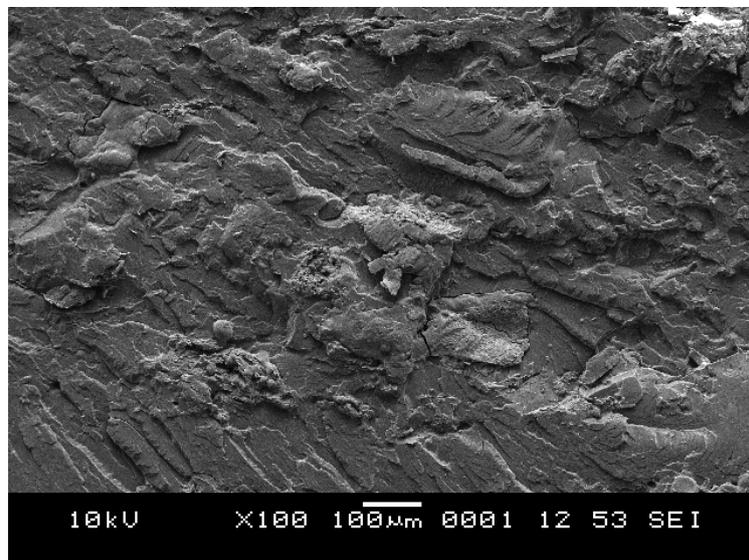


Fig. 3.8 The SEM micrograph of tensile fracture surface of compatibilized biocomposite (40 php corn cob).

4. Conclusion

The tensile strength and elongation at break of PP/CC biocomposites decreased with increasing corn cob loading while modulus of elasticity increased. The compatibilized biocomposites have higher tensile strength and modulus of elasticity compared to the uncompatibilized biocomposites. The incorporation of compatibilizer proved to be effective in enhancing the compatibility of a system comprising of hydrophilic corn cob filler and hydrophobic polypropylene. The morphology study indicates that the interfacial adhesion between corn cob and PP matrix was enhanced with MAPP as compatibilizer.

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