

Modified Polyethylene for Synthetic Wood Applications

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Polyethylene as a polyolefin has been grafted with maleic anhydride under optimized conditions to attain maleic anhydride grafted polyethylene with higher grafting yield. Maleic anhydride grafted polyethylene has been characterized with FT-IR spectroscopy and thermal analysis as well as some chemical tests. A suitable amount of saw dust as an example for natural fibers has been collected and prepared for hot press casting with polyethylene to attain wood plastic composite. Maleic anhydride grafted polyethylene was used as a coupling agent to enhance the compatibility between polyethylene and saw dust. Samples of wood plastic composite were prepared without maleic anhydride grafted polyethylene as blank. Wood plastic composite samples have been tested regarding mechanical, physical and chemical characteristics.

Keywords: Modification, Natural Fiber, Grafting, Polyolefins, Wood, Tensile Strength.

INTRODUCTION

Modification of polymers is a well known strategy to change the characteristics of the polymer according to the modification technique and extent to be suitable for the application field¹⁻⁶. Composites are materials consisting of two or more identifiable constituents but not mixed to an atomic scale⁷ and are controlled by the properties of their individual compositions and interaction. The major constituents of wood-plastic composites are both the filler which is either wood or generally natural fibers and the matrix which can be thermoset or thermoplastic resins in addition to other chemical additives. The use of fillers in thermoplastic industry is a common way to increase stiffness and strength to plastics. Inorganic fillers are of the greatest in demand especially calcium carbonate, glass fiber, clay, talc and mica. The supposed environmentally friendly nature of organic fillers has attracted the industry and has led to a major shift in choosing filler types. The growth of wood plastic composites has shown a jump during the last two decades in the plastic industry and the acceptance of wood plastic composites which are currently used in various applications such as decking, roof tiles, siding, window and door frames attracted the attention of industry to the organic fillers⁸.

Numerous studies over the past decades on wood fiber plastic composites indicated that composites can be readily formed using compounding and compression molding technologies⁹. In most of those technologies, wood fiber either

mixed with polymer or added as filler in it followed by pressing or molding under suitable conditions of pressure and temperature. Although different compounding techniques can be applied to produce wood plastic composites, twin screw extruder is still the standard in the industry resulting in production of high modulus composite with low rate of water absorption. However, there is no much investigation to know the effect of extrusion variables on characteristics of wood plastic composites¹⁰⁻¹³. wood plastic composite covers several composites using polyolefins such as polypropylene, poly(vinyl chloride) and polyethylene and binders or fillers such as wood flour, flax fibers and other natural fibers¹⁴. Wood is a lignocellulosic material composed mainly of cellulose (50-65 %), reasonable content of lignin (20-25 %) in addition to some extractives and traces of ash (1-10 %). The ratio of constituents differs based on species of wood¹⁵.

At the beginning, wood plastic composite was formed by using recycled wood fibers or chips. Unfortunately, such composites products were ideal for relatively less demanding applications but there are increased efforts to produce wood plastic composites as a viable alternate use for residual plant fiber material and thermoplastics¹⁶⁻²². The new generations of wood plastic composites are high-end technology products which exhibit superior mechanical properties, high dimensional stability and can be extruded to high dimensional tolerances²³. This helps to form tough and stable complex shapes needed for engineering applications⁸.

The advantages of wood plastic composites are their processing ability; wide range and inexpensive raw materials which can be wastes of wood and recycled plastics and their competitive price with conventional supplies such as medium density fiberboard and PVC in addition to their availability in several finishes and appearances. Hence, wastes of wood and recycled plastics become useful resources by converting them into wood plastic composite instead of causing environmental concerns. Despite the advantages of wood plastic composite over wood and plastic, the interaction between wood and plastic at fiber-matrix interface does not necessarily yield strong bonds²⁴. The major reason for weak bonds has been attributed to the polar nature of the wood (hydroxyl groups) while some plastics such as polyethylene and polypropylene are non-polar polymers²⁵. It is necessary to modify the wood fiber with a proper coupling agents or coating the fiber with appropriate surface modifying resin to develop composites with superior bonds at the boundary which is a significant factor to obtain composites of improved mechanical properties²⁶. The other alternative is to modify the plastic component in the wood plastic composite either by using blends with different plastic types or by using coupling agent which may be compatible with the hydrophobic plastic components and the hydrophilic wood or natural fiber component. In such cases grafted polypropylene and/or polyethylene with maleic anhydride can be of benefits in this regard²⁷.

EXPERIMENTAL

All chemicals are purchased by Aldrich unless otherwise mentioned. Thermal and FT-IR Spectroscopic analyses used for characterization of maleic anhydride grafted polyethylene were achieved in the department. Tensile testing has been also performed in the Faculty of Engineering, King Abdulaziz University at Saudi Arabia.

Preparation of maleic anhydride grafted polyethylene: A mixture of 70 g of polyethylene (2.5 mole), 49 g of maleic anhydride (0.5 mole) and 1.2 g of benzoylperoxide (5 mmole) was added to 250 mL of benzene. The mixture was kept under reflux with stirring for 2 h and then left to cool while stirring until the temperature reduced to 60 °C. The reaction mixture has been poured onto a large amount of ethanol while stirring. The obtained product has been collected by filtration, air dried at 50 °C under reduced pressure and prepared for characterization by using FT-IR spectroscopic analysis.

Sample preparation: Saw dust used as reinforcing material was a mixture of different wood species collected from public carpentries in Jeddah, Saudi Arabia with particle size ranged between 80-100 mesh. Commercial polyethylene produced by the Saudi Basic Industrial Corp. (SABIC), Saudi Arabia was converted into small particles. A maleated polyethylene (MAPE) was prepared by grafting of polyethylene with maleic anhydride as mentioned above and used as a coupling agent.

Compounding: Saw dust was dried at 40 °C under reduced pressure for 24 h to moisture content of about 2 % and then kept in sealed bags until required. The different samples were prepared as pellets through melt blending, extrusion and palletizing at 120 °C using a laboratory size twin-screw extruder. The test specimens were obtained by melt press molding of the obtained pellets after drying at 80 °C for 24 h. All samples were melt press molded using a melt press of 10 kN/cm². Table-1 shows the composition of samples with saw dust content up to 45 % based on the total weight of the mixture prior to compounding and in presence of 5 % maleic anhydride grafted polyethylene as a coupling agent.

TABLE-1				
COMPOSITION (%) OF THE POLYETHYLENE-SAW				
DUST BLENDS				
Comment	\mathbf{C}			

Component		Composition (%)					
Polyethylene	100	95	85	75	55		
Saw dust	0	5	15	25	45		
Maleic anhydride grafted polyethylene	5	5	5	5	5		

FT-IR spectroscopic analysis: Samples of polyethylene, maleic anhydride and maleic anhydride grafted polyethylene have been characterized by using FT-IR Spectroscopic analysis. The spectra of the above mentioned samples are shown in Fig. 1.

Thermal analysis: Samples of polyethylene, saw dust and wood plastic composite have been characterized by using thermo-gravimetric analysis (DTG) in air and with heating rate of 10 °C/min. Results are shown in Figs. 2-4.

Tensile strength measurements: Tensile strength was measured for polyethylene-saw dust wood plastic composite samples with a Universal Testing Machine at the Faculty of Engineering, KAU, Saudi Arabia. Test specimens were of W = 19 mm, L = 115 mm and T = 3.5 mm dimensions as shown in Fig. 5 and the tests were conducted at a speed of 100 mm/min. Fig. 6 shows the average values of 5 replicates for each condition to obtain more representative results.

RESULTS AND DISCUSSION

There are different ways for grafting of polyethylene with maleic anhydride including melt extrusion in presence of a suitable initiator. This way has some drawbacks in the light of the processing ability of the grafting mixture during extrusion. In the current work, maleic anhydride has been grafted onto polyethylene using benzene as a liquid phase to facilitate good distribution of maleic anhydride over the amount of polyethylene to be grafted. Moreover, conducting the grafting process in presence of benzene keeps the ambient temperature low and consequently the adverse effect of higher temperature during the extrusion will be minimized.

FT-IR spectroscopy of maleic anhydride grafted polyethylene: Grafting of maleic anhydride onto polyethylene chains was confirmed by FT-IR spectroscopy and the relative percentage of maleic anhydride grafting in maleic anhydride grafted polyethylene can be predicted. FTIR spectra were recorded from 5000 to 400 cm⁻¹. The relative under-peak area of the anhydride absorption between 1860 and 1710 cm⁻¹ to the CH stretching peak at 720 cm⁻¹ was considered as an approximate indicator for the grafting extent of maleic anhydride.

Samples were prepared by hot press under 10 kN force at 200 °C to form thin films. Fig. 1 shows the FTIR spectra of maleic anhydride grafted polyethylene in addition to those of polyethylene and maleic anhydride for comparison. It is

obvious from this figure the presence of new peaks 1720 and 1787 cm⁻¹ when maleic anhydride is grafted successfully onto polyethylene. The bands at 1787 and 1720 cm⁻¹ are due to the asymmetric and symmetric stretching modes, respectively, of carbonyl (C=O) groups of saturated maleic anhydride residues grafted onto polyethylene²⁸⁻³⁰.



Fig. 1. FT-IR spectra of polyethylene, maleic anhydride and maleic anhydride grafted polyethylene

Thermal analysis: It is known that T_g of polyethylene is about 20 °C and the melting temperature (T_m) is 130 °C. Also the ash ignition temperature is 340 °C while the self-ignition temperature in air is 350 °C. In the current study, polyethylene sample was heated in air. Fig. 2 shows that the endothermic peaks occur around 138 °C. Fig. 3 shows the thermal analysis data of the saw dust in air where an endothermic peak occurs around 355 °C representing thermal degradation. There are also two exothermic peaks observed around 328 °C and 445 °C resulting from combustion.







Fig. 3. TG-DTG plot of polyethylene in air at heating rate of 10 °C/min

Fig. 4 shows the TG-DTG plots of wood plastic composite composed of polyethylene and saw dust where the peak at 315 °C results mainly from polyethylene while that at 355 °C results from both polyethylene and saw dust. In addition, there is a peak at 435 °C which corresponds to polyethylene only. This means that the addition of saw dust facilitates the oxidation and combustion since wood is more combustible than polyethylene.



Fig. 4. TG-DTG of wood plastic composite sample in air at heating rate of 10 °C/min

Tensile strength: Wood plastic composite samples used for tensile testing were of the dimensions W = 19 mm, L = 115 mm and T = 3.5 mm as shown in Fig. 5. Tests were conducted by using of a universal tensile testing machine at a speed of 100 mm/min for 5 replicates.

Blank samples of wood plastic composite with no maleic anhydride grafted polyethylene showed tensile strength lower than those containing maleic anhydride grafted polyethylene as coupling agent. This behaviour was shown by all samples of different saw dust contents up to 45 %. The maximum tensile strength for the blank samples was 38.02 N/mm² while it was 52.06 N/mm² for the samples with maleic anhydride grafted polyethylene as coupling agent as shown in Fig. 6. This reflects



Fig. 5. Dimensions in mm of wood plastic composite test specimens for tensile strength test. Sample thickness for mechanical tests = 3.5 mm

the great impact of maleic anhydride grafted polyethylene on the compatibility of wood plastic composite components.

Fig. 6 shows the dependence of tensile characteristics on the content (wt %) of saw dust in presence of 5 % of maleic anhydride grafted polyethylene as coupling agent and in absence of maleic anhydride grafted polyethylene as a blank. The tensile strength of the blank was 38.02 N/mm^2 at 0 % saw dust content and decreased by increasing the saw dust content of the sample up to 45 wt % leading to decrease of the tensile strength to 34.32 N/mm^2 . This means that the addition of saw dust up to 45 wt % leads to reduction in the tensile strength of 9.7 % in comparison with pure polyethylene. This is attributable to the incompatibility of the hydrophobic polyethylene with saw dust which contains hydrophilic functionalities. This has been reflected as a decrease in the bonding strength between polyethylene and saw dust.

On the other hand, samples with maleic anhydride grafted polyethylene as coupling agent showed tensile strength of 39 N/mm² at 0 % saw dust content and increased up to 52.06 N/mm² at 45 wt % of saw dust as shown in Fig. 6. It is obvious that the addition of maleic anhydride grafted polyethylene significantly increased the tensile strength almost in linear manner. This can be attributed to a stronger bonding between polyethylene and saw dust in presence of maleic anhydride grafted polyethylene as coupling agent which contains both hydrophobic and hydrophilic natures represented by polyethylene chains and maleic anhydride functionality added through grafting.



Fig. 6. Tensile strength and tensile modulus of wood plastic composite samples

Conclusion

From the current study, it can be concluded that the modification of polyethylene with maleic anhydride leads to promising materials derived from the different inexpensive polyolefins available in the market as waste material. The modified polyolefins serve as good candidates to attain better compatibility with natural fibers depending on the application directions. The tensile strength decreased with increasing saw dust due to the weak bonding with polyethylene. Utilization of maleic anhydride grafted polyethylene increased the tensile strength in comparison with pure polyethylene.

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