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Influence of Ethylene-Glycidyl Methacrylate (EGMA) on TGA-FTIR Analysis of Recycled Polymer Blends and High Loading Biocomposite

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Abstract – *The recycled polymer blends based on recycled high density polyethylene (rHDPE) and recycled poly (ethylene terephthalate) (rPET) at 75/25 wt% with and without 5% EGMA was prepared in a co-rotating twin screw extruder. The effects of adding 5% EGMA on the compatibility of biocomposite a high loading of rice husk (RH) were also investigated. Maleic anhydride polyethylene (MAPE) was used in biocomposite as a coupling agent to increase the adhesion of the fiber–matrix interface. The TGA result showed the addition of rice husk and EGMA increased the degradation temperature and thermal stability of the materials. FTIR analysis of the biocomposite confirmed the chemical interaction and interfacial bonding between the two phases. From these results, we can conclude that ethylene-glycidyl methacrylate (E-GMA) copolymer improved the compatibility of the immiscible composites.* ***Copyright © 2015 Penerbit Akademia Baru - All rights reserved.***

Keywords: Recycled polymer blend; Rice husk; TGA; FTIR analysis

1.0 INTRODUCTION

The invention of new biocomposites consisting of recycled materials with post-consumer polymers as matrices and agro-waste fibers as reinforcement phases, and a better understanding of the fiber–matrix interaction will increase the aggregate values and applications. Therefore, the development will reduce the environmental impact, close the carbon cycle and produce a green composite [1].

Rice husk (RH), a kind of natural fiber, is an agricultural, industrial waste generated during the rice milling process in rice-producing countries, especially in the Asian, Pacific and North American regions [2]. In Malaysia, about 680,000 hectares of land are designated for paddy planting, from which a total of 840,000 tons of RH is produced annually [3]. The raw RH contains 25–35% cellulose, 18–21% hemicellulose, 26–31% linen, 15–17% silica, 2–5% soluble and 7.5% moisture content [4]. The reasons behind the use of RH in the composite material industry are its low cost, high availability, low bulk density (90–150 kg/m3), toughness, abrasive nature, resistance to weathering, renewability, biodegradability and non-hazard [5].

HDPE and PET are widely used in the packaging industry, and their annual rates of consumption keep increasing [6]. Blends of HDPE / PET does not demand to be dried before processing and have properties intermediate between these two types of plastic components. Compared to PET, they are less brittle; while compared with HDPE, they are stiffer with better cooling and flowing. On the topic of the written report before this HDPE / PET blends, most researchers have concentrated on the compatibilization methodologies since HDPE and PET compatible in nature because of the big divergence in the solubility parameter between them [7, 8].

The incorporation of a surface-active species called compatibilizer which concentrates on the interface, tends to improve the interfacial adhesion as well as refined and stabilize the blend morphology. Maleic anhydride polyethylene (MAPE) is often used for polyethylene (PE) composites that are filled with lignocellulosic materials [9]. The anhydride group of MAPE tends with chemically link with the hydroxyl group (hydrophilic) of lignocellulosic filler, on one side, whereas the ethylene blocks of MAPE facilitate the wetting of the hydrophobic polymer chains, on the other side [10, 11]. There are three main chemical aspect reasons for that statement. GMA-containing copolymers are the most efficient species as compatibilizer. First, the epoxy functionality of GMA able to react with both hydroxyl and carbonyl end groups of PET, whereas the MA reacts only with hydroxyl ends. Second, epoxy function of GMA has higher reactivity than MA towards hydroxyl groups of PET It has been shown that ethylene-glycidyl methacrylate (E-GMA) copolymer is the most effective compatibilizer to improve the compatibility between the hydrophobic HDPE and hydrophilic PET, and, hence, enhance the properties of the blends [8]

The aim of this study was to investigate and compare the interfacial adhesion by using TGA and FTIR techniques when applying EGMA as a compatibilizer on the blends.

2.0 METHODOLOGY

2.1 Raw Materials

The polymer matrices investigated in this study included recycled high-density polyethylene (rHDPE) as the main phase (matrix) and the recycled polyethylene terephthalate (rPET) as the minor (dispersed) phase. Both of rHDPE and rPET were obtained from a local plastic recycling plant, which were derived from post-consumer plastic wastes. An E-GMA copolymer, Lotader AX8840 with a melt index of 5 g/10 min (190 °C, 2.16 kg) with a GMA content of 8%, was used as a compatibilizing agent for PBs. RHF and MAPE were used as filler and coupling agents for RH reinforced composites, respectively. RH was dried in an oven at 100 °C for 24 h before use. All the raw materials were obtained from the plants, namely BioComposites Extrusion Sdn. Bhd.

2.2 Preparation of the Composites

The samples of RH reinforced recycled polymer blend were grown in a two-stage process. The raw materials are first formulated tumble-mixed before melt-blended through extrusion. In the first extrusion, the polymer blend pellets by rHDPE and rPET has been made in a laboratory scale co-rotating twin screw extruder (Thermo Prism TSE 16 PC). The four barrel temperatures from the feeding to die zones were set as 250, 270, 240 and 190°C and the speed rotary screw was set at 30 r/min. The weight ratio of rHDPE/rPET/E-GMA was fixed at 75/25 (wt/wt) with and without 5% EGMA. The extrudates were cooled and granulated into pellets by a crusher. The blend pellets were dried at 100 °C for 24 h before use. In the second extrusion, the polymer blend pellets were melt blended with dried RH with a temperature profile of 195 °C, 215 °C, 210 °C and 190 °C. The screw speed was 40 r/min. The RH to the plastic weight ratio was 70/30 (wt/wt). The MAPE loading level was set at 3% based on the total weight of composites. The extrudates were cooled and granulated into pellets.

2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851^e on 10–15 mg samples. Samples of TGA were tested at a heating rate of 10 °C/min over the temperature range from 25°C to 600°C, the temperature of complete degradation.

2.4 FTIR Analysis

The infrared spectra in the FTIR-ATR of composites were obtained using a FTIR-Near Infra Red with imaging system (Perkin Elmer Spectrum 400 FT-IR). The samples were analyzed over the range of 650-4000 cm^{-1}. This analysis of the blends was performed at point-to-point contact with a pressure device.

3.0 RESULTS AND DISCUSSION

Figure 1 and 2 shows the thermogravimetric curves of rHDPE,rPET, rice husk, rHDPE/rPET and biocomposites with and without 5% EGMA as a compatibilizer. The thermal degradation of rHDPE started at 375 °C, maximum decomposition rate occurred at about 470 °C and 100% degradation are detected at 600 °C (Table 1). The neat rHDPE clearly illustrate higher thermal stability than the neat rPET; which indicates the least thermal stability compare to rHDPE. rHDPE decomposes into a large number of paraffinic and olefinic compounds without residue [12, 13]. The rHDPE/rPET blend (rMatrix), with or without EGMA, exhibits thermal stability between the neat rPET. Of the two blends, that with EGMA blend shows lower stability, because the thermal stability of EGMA (with unsaturated double bonds) is less than that of PP/HDPE blend. The thermogravimetric curve of rice husk exhibits two mass loss steps. The initial mass loss below 100 °C is due to the gradual evaporation of absorbed moisture and the second mass loss of approximately 170 to 350 °C is due to the decomposition of the three major constituents of the natural filler (hemicelluloses, cellulose, and lignin) [14, 15]. A residue of around 35 wt % is observed for rice husk at 600 °C and it is basically silica [15, 16]. The maximum temperature of degradation is seen to increase with adding rPET and RH content. The incorporation of RH into the blend greatly enhanced the blend’s thermal stability, and a RH with EGMA loading leads to a slightly superior thermal stability. The variation increases in the presence of the EGMA showing that there is a marginal improvement in thermal stability in addition of compatibilizer. The addition of rice husk into polymer blends increases this to 477 °C - 485 °C. Improved thermal stability of the composites rice husk is caused by the interaction of organic / inorganic, between polymer and rice husk (RH) where inorganic filler delay volatilizations of products produced at a temperature of carbon-carbon bond scission polymer matrix [12]. The presence of filler restricts the mobility of the polymer chains and thus slow down the thermal degradation. Compatibilized blends showed slightly superior thermal stability is reduced by virtue of the motion segment of the polymer chain. This has the effect of making less mobile chain caused by the interaction between the matrix and RH. This has the effect of making the blend less susceptible to thermal degradation [12]. The composites with EGMA showed a different percentage of residue after 600 °C associated with the two elements of the composite, with increase the percentage of residue to 28.5%, indicates the thermal stability.

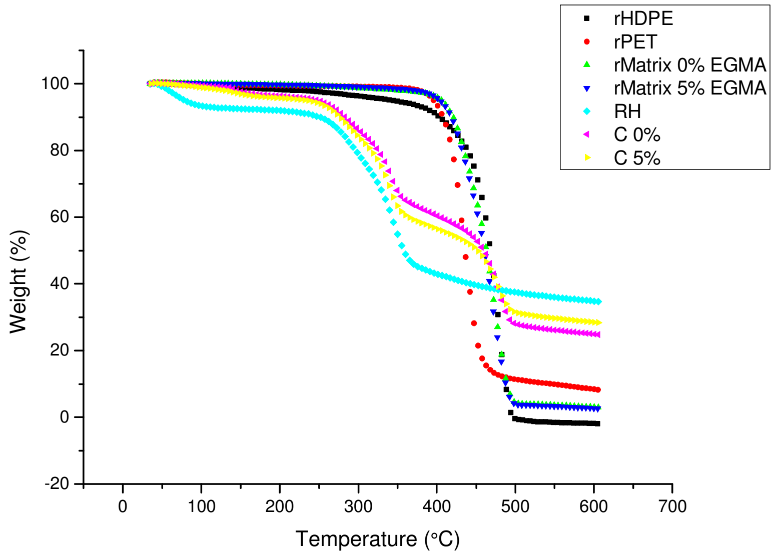

Figure 1: TGA thermographs of rHDPE, rPET, rMatrix without EGMA, rMatrix with 5% EGMA, rice husk (RH), biocomposite without EGMA (C 0%) and biocomposite with 5% EGMA (C 5%)

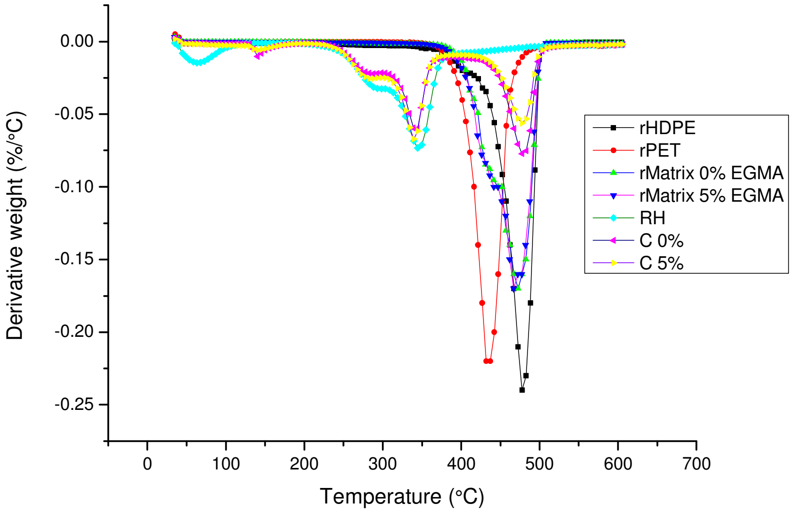

Figure 2: DTG thermographs of rHDPE, rPET, rMatrix without EGMA, rMatrix with 5% EGMA, rice husk (RH), biocomposite without EGMA (C 0%) and biocomposite with 5% EGMA (C 5%)

Table 1: Thermogravimetric data

Sample	Onset Temperature (°C)	Peak Temperature (°C)	Residue after 600 °C (%)
rHDPE	375	470	0
rPET	359	431	8.37
RH	170	1st peak 293 2nd peak 344	34
rM 0% EGMA	328	472	3
rM 5% EGMA	343	467	2.74
C 0% EGMA	215	1st peak 339 2nd peak 477	24.8
C 5% EGMA	195	1st peak 339 2nd peak 485	28.5

Figure 3 illustrates FTIR spectra of biocomposites with and without 5 % EGMA. The peak at 2916 cm-1 is assigned to CH stretching in $-CH_2-$ groups. The peak at around 2916 cm^{-1} in the spectra is probably associated with the (CH) stretching of cellulose fiber [17]. The peak at 2916 cm^{-1} appeared as a very strong peak in composite without EGMA and a much weaker peak in composite with EGMA, relatively large proportion of HDPE consisted of $-CH_2-$ groups. The C=O stretching of the ester group in EGMA was seen by the appearance of absorption band at 1717 cm^{-1}. The peak at 1023 cm^{-1} is associated with both the C-O stretch in cellulose and the C-O deformation in the primary alcohols of lignin [18, 19]. The IR spectrum of the RH shows absorption bands in the region near 1717 cm^{-1}. This absorption band may be due to the carboxyl group of acetyl ester in hemicellulose and carboxyl aldehyde of lignin. The band placed at 1717 cm^{-1} in the spectrum of composites is attributed to C=O stretching of the acetyl and uronic ester groups of hemicellulose or the ester linkage of carboxylic groups of ferulic and p-coumaric acids of lignin and/or hemicellulose. This band has present with high intensity in the FTIR spectra of composites without EGMA indicated that hemicellulose and lignin were not completely removed [20]. Absorption peak at 1462 cm^{-1} was attributed to the CH_2 bending of cellulose and the absorption band at the region around 3450 cm^{-1} was related to the hydroxyl group (-OH). The absorption peak of composite with EGMA around 3450 cm^{-1} was found to be broader compared to composite without EGMA. This was due to the presence of -OH groups in large amount after compatibilized on the composite that caused the peak to become broader compared to uncompatibilized [17]. The band at 1249 cm $^{-1}$ corresponds to C-O-C (aryl-alkyl ether). These peak discribe that EGMA will effectively interacted with lignin. This peak intensity reduces after adding EGMA. MA treated fiber also showed a narrower absorption peak around 3435 cm^{-1} and shows that the amount of free hydroxyl groups were lower. The absorbance peaks are at 1717 cm^{-1}, which was attributed to MA symmetric C=O stretching of MAPE. This result suggests that MAPE interaction with RH by forming a covalent linkage and ester bonding between the MA Group of MAPE and the hydroxyl groups on the RH surface, as well [21]. This effect was clearly supported by the special peaks that is evident at 1717 cm^{-1}, which may have ensured from the esterification of the hydroxyl groups and the resultant increased stretching vibration of the carbonyl groups (C=O) [21-23]. Therefore, the bonding of composites offers better wettability and dispersion, which can thereby improve the properties of the complexes.

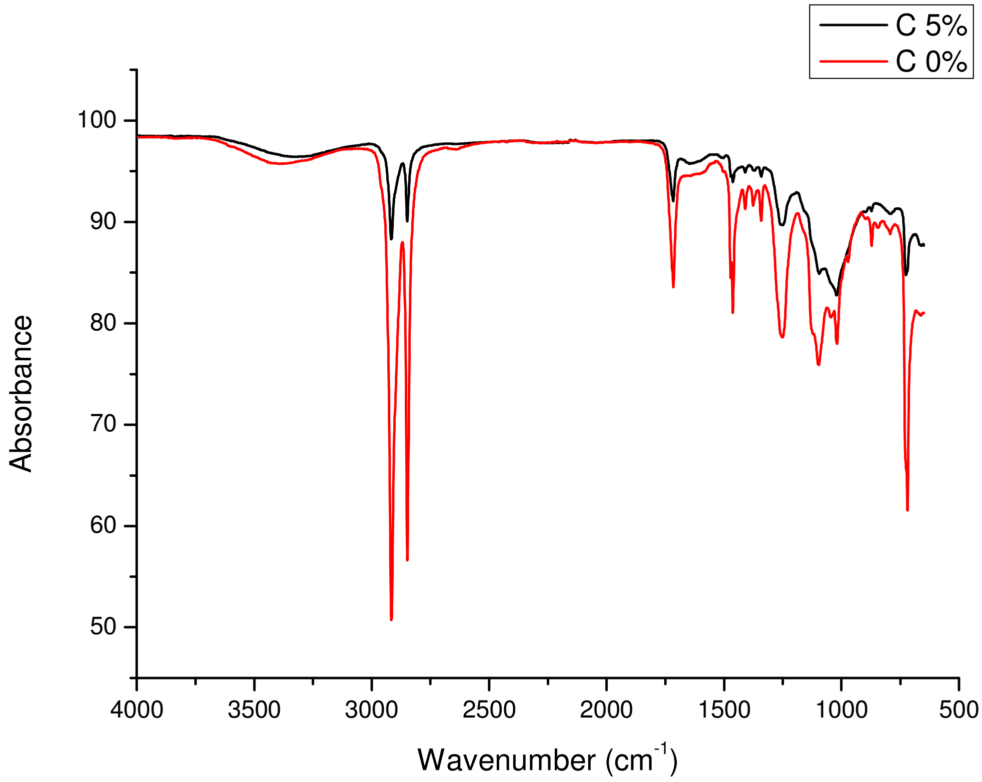

Figure 3: FTIR spectra of uncompatibilized and compatibilized composites with EGMA

Table 2: Assignment of FTIR peaks for specific group

Band position (cm^{-1})	Assignments
3450	-OH
2916	C-H stretching; $-CH_2-$
2848	C-H stretching
1717	C=O stretching; R(C=O)OH
1462	C-H bending; $-CH_2-$
1249	C-O-C (aryl-alkyl ether)
1023	C-O stretching
725	C-H rocking; $-CH_2-$

4.0 CONCLUSIONS

The blends were prepared via melt blending for the investigation of thermal and chemical stability. Recycled matrices with rice husk were chemically treated with MAPE in order to improve the compatibility between the hydrophilic RH and hydrophobic matrix. Influence of adding EGMA was investigated through TGA and FTIR analysis. The compatibilized blends show a good thermal stability with the peak temperature at 485 °C and 28.5% of residue at 600 °C that give the essence of producing the blend less receptive to thermal degradation. The application of EGMA was proven to be efficacious in increasing the interactions between two phases progressively and enhancing the phase dispersion of the blends. This was supported by the FTIR results that the absorption peak of composite with EGMA around 3450 cm^{-1} was found to be broader, the weaker peak at 2916 cm^{-1} and 1023 cm^{-1} demonstrate the EGMA copolymer improved the compatibility of the immiscible composites.

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