

NATURAL FILLERS-FILLED STYRENE MALEIC ANHYDRIDE COPOLYMER COMPOSITES

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ABSTRACT

The aim of this study was to determine morphological characterization, mechanical properties and thermal stability of natural fillers-filled styrene maleic anhydride (SMA) copolymer composites. SMA and natural fillers including starch, α -cellulose, and ultra-fine cellulose (UFC) were used to manufacture composites in thermal melting mixer. The morphology of natural fillers-filled SMA composites was investigated by scanning electron microscopy (SEM). It was observed that natural fillers were dispersed within SMA matrix and there were some voids in the composites. It can be said that the voids occurred due to esterification reactions between matrix and fillers. Mechanical properties of the composites were determined with flexure test, tensile test and impact test. The results were showed that flexure and tensile strength and impact strength were decrease as adding the particles; whereas, both flexure and tensile modulus of elasticity (MOE) were increased to SMA/AC and then decreased to both SMA/UFC and SMA/Starch. Thermal stabilities of the composites were measured by thermogravimetric analysis (TGA) and it was found that thermal stability of the composites was lower than the neat SMA. The interaction between SMA and natural fillers was studied by Fourier transform infrared spectroscopy (FTIR). It was said that FTIR curves of the composites generally were same to each one.

KEYWORDS: Styrene maleic anhydride copolymer, natural fillers, thermal stability, mechanical properties, morphological analysis.

INTRODUCTION

Natural particles are abundant, cheap, renewable and sustainable raw materials. They are used in the many industry such as furniture, panel manufacturing, different composite, etc.

In recent years, the use of natural fibers as reinforcements in polymers and composites has attracted much attention due to the environmental concerns (Kishi et al. 1988; Maldas et al. 1988; Woodhams et al. 1984; Yam et al. 1990). Wood, cellulosic fiber/particles, sisal, jute in their natural condition, as well as, several waste cellulosic products such as shell flour, wood flour, potatoes/corn starch and pulp have been used as reinforcement agents of different thermosetting and thermoplastic resins. These biomasses have many properties which make them an attractive alternative to traditional materials (Simonsen et al. 1998, Oksman et al. 1998). They have high specific properties such as stiffness (George et al. 2001), flexibility (Ahlblad et al. 1994), and modulus (Geethamma et al. 1995). In addition, they are available in large amounts (Hornsby et al. 1997), and are renewable and biodegradable. Other desirable properties include low cost, low density, less equipment abrasion (Ahlblad et al. 1994, Mi et al. 1997), less skin and respiratory irritation (Coutinho et al. 1997), vibration damping (George et al. 2001, Varghese et al. 1994), and enhanced energy recovery (Coutinho et al. 1997, Oksman et al. 1998). The biomass could be profitably used in the manufacture of polymer matrix composites because they possess attractive physical and mechanical properties (Cazaurang-Martinez 1991). They impart the composite high specific stiffness and strength, a desirable fiber aspect ratio, biodegradability, they are readily available from natural sources and more importantly they have a low cost per unit volume basis. It should also be mentioned that the hollow nature of vegetable fibers may impart acoustic insulation or damping properties to certain types of matrices.

Both synthetic and natural polymers play an essential and ubiquitous role in everyday life because of their broad range of properties (McCrum et al. 1997; Painter et al. 1997). They are studied in the work fields such as agriculture, medicine, industry, etc. In this study, styrene maleic anhydride (SMA) co-polymer commonly used in the automotive industry was selected to produce the cellulosic composites. The automotive industry uses styrene-maleic anhydride (SMA) copolymers for the injection molding and thermoforming of interior parts (Painter et al. 1997). The maleic anhydride functionality improves the properties of the copolymer and maleic anhydride groups in the SMA begin to start the esterification reaction with cellulosic biomass having hydroxyl groups. Thus, mechanical properties of the composites obtained can be improved.

It is extremely important to have information about the impact of high processing temperatures during the manufacturing of natural fillers reinforced composite materials with SMA. Natural fillers might be degraded and its mechanical and thermo-mechanical properties decreased during high melt temperature processing (Aydemir et al. 2014a; 2014b; Kiziltas et al. 2011a; Aydemir et al. 2015). The aim of this study was to investigate the effects of natural fillers on the morphology, mechanical and thermal properties of SMA composites.

MATERIAL AND METHODS

Material

Styrene maleic anhydride copolymer having 1.08 g.cm⁻³ density; 10 % of maleic anhydride content was supplied by Nova Chemicals. Alpha cellulose (AC), ultra-fine cellulose (UFC) and potato starch (PS) was used as the reinforcement for the polymer composite. AC and UFC were supplied by Rettenmaier & Sohne (JRS) with 70-120 μm and 200-1000 nm particle size respectively. The PS, trade name S 4251, was supplied by Sigma Aldrich Co., USA. All reinforcing fillers were stored in sealed containers after being oven dried for at least 16 hours at 105°C to obtain moisture content less than 1 percent.

Preparing of the composites

The SMA was mixed with the natural fillers by thermal compounding using a Brabender Prep-mixer[®] equipped with a bowl mixer and the process temperature and torque changes were measured in real time. The sample formulations used are listed in Tab. 1. Experimental parameters used during thermal compounding were 200-220 for mixer temperature, 210-220°C for melting temperature, and 60 rpm for rotor speed. The procedures of the experiments were as follows; the mixer was started at 60 rpm when the reaction chamber was heated to 220°C. SMA pellets were first fed into the chamber, after five minutes the polymer was completely melted; the mixture of particles was slowly added to the SMA melt. The system was kept closed to five seconds after the fillers were added with the SMA matrix. The thermal mixer was stopped and then the blending obtained was removed from the mixing system.

Tab. 1: The sample formulations for bench scale compounding.

Polymer matrix	Fillers	SMA
SMA	-	100
SMA/AC	30	70
SMA/Starch	30	70
SMA/UFC	30	70

The blending obtained was grinded and then granules obtained were used to injection molding. The samples were dried at 105°C for 16 hours. Test samples were prepared with injection molding at 220°C; injection pressures varied from 8.3 to 12.4 MPa, depending upon the compound.

Methods

Tensile tests were conducted according to ASTM D 638-03 (2003). The tensile behaviors of composites were measured using an Instron 8801 with a 5 kN load cell. All the tension tests were conducted at a rate of 5.08 mm.min⁻¹. Flexural tests were conducted according to ASTM D 790-07 (2010). This test consisted of a three-point loading system introducing mid-span loading using an Instron 8801 with a 225 N load cell. The support span was 50 mm, resulting in a span-to-depth ratio of 16 (± 1). All flexural tests were conducted at a rate of 1.27 mm.min⁻¹. Impact tests were conducted according to ASTM D 256-06 (2011). The notches were added using a NotchVIS machine manufactured by Ceast. The samples were tested on a Resil 50 B impact test machine, manufactured by Ceast. At least six samples were tested for each composition and the results are presented as an average for tested samples.

TGA measurements were carried out using a Mettler Toledo analyzer on 10 mg samples. Each sample was scanned over a temperature range from room temperature to 600°C at a heating rate of 10°C.min⁻¹ under a 20 ml.min⁻¹ nitrogen flow rate to avoid sample oxidation. The samples used for the TGA measurements were randomly picked 5 individual samples from ground samples. Scanning electron microscopy (SEM) was used to characterize the morphological properties in the composites. The samples were frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact. Subsequent gold coating provided the necessary conductive surface for the electron microscope.

The morphology study was performed on AMR 1000 scanning electron microscope. The changes in chemical structure and binding configuration of a thin layer were analyzed by attenuated total reflectance (ATR) spectroscopy. ATR-FTIR spectra were recorded in the wave number range 4000–600 cm⁻¹ by the compensation method. Spectra were recorded on a

Perkin Elmer FT-IR Spectrum GX spectrophotometer (USA) by averaging 64 scans at room temperature.

RESULTS AND DISCUSSION

Mechanical properties of the SMA matrix composites were given in Figs. 1, 2 and 3.

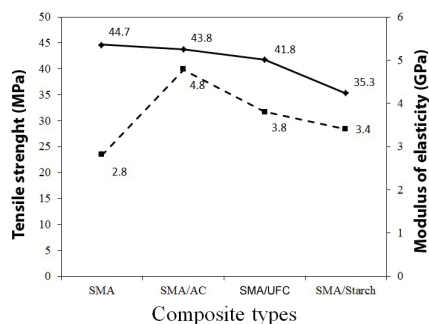


Fig. 1: Tensile strength and modulus of elasticity (TMOE) of natural fillers reinforced SMA composites.

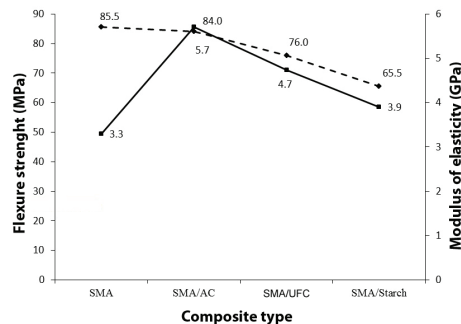


Fig. 2: Flexure strength and modulus of elasticity (FMOE) of natural fillers reinforced SMA composites.

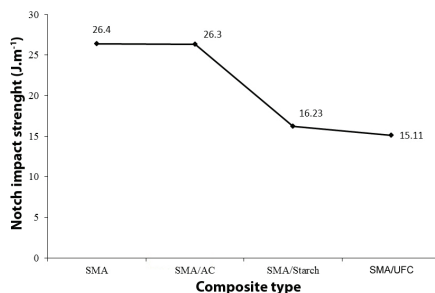


Fig. 3: Notch impact strength of natural fillers reinforced SMA composites.

Fig. 1 shows tensile strength and tensile modulus of elasticity of the SMA matrix composites. Tensile strength decreased with adding of particles. The minimum tensile strength of the composites was found as 35.3 MPa (decreasing ratio is 21.1 %) to starch/SMA composites. The results showed that adding of particles have a negative effect on the properties of SMA composites. Tensile modulus of elasticity (TMOE) increased with adding of particles and the maximum elasticity of modulus was found to be in the composites with AC. It can be said that adding of natural fillers has a positive effect on TMOE for SMA composites.

Fig. 2 shows flexure strength and flexure elasticity (FMOE) of the SMA matrix composites. Adding of natural fillers decreased the flexure strength of the composites. The minimum flexure strength of the composites was determined as 65.5 MPa to Starch filled SMA composites. Natural fillers have an increasing effect on FMOE of the composites. The maximum and minimum modulus of elasticity was found as 5.7 and 4.7 GPa. It can be said that the trends in the flexure test were similar to tensile test. Simonsen et al. (1998) studied in SMA prepared with

aspen fiber, wood flour and old newspaper. The results obtained that adding of particle for 10 and 20 % increased the flexure strength, but tensile strength decreased with adding of particle for 30 %. It was determined that this leveling off of MOR maybe due to the presumably high surface-area fillers that was not completely wetted by the matrix polymer. The study showed that MOE increased with adding of filler.

Fig. 3 shows the notch impact strength of the SMA matrix composites. Adding of alpha cellulose didn't change the impact strength of pure SMA. But, UFC and starch decreased the impact strength. Simonsen et al. (1998) worked properties of natural filler reinforced SMA composites. The diminution in impact strength seemed to be greatest as the filler content rose from 0 to 20 percent. The further decreases with in creasing filler content were found to be less severe. The mechanical properties of composites depend of the distribution of particles in matrix. Therefore, Morphological characterization of the composites was investigated with helping of SEM in Fig. 4.

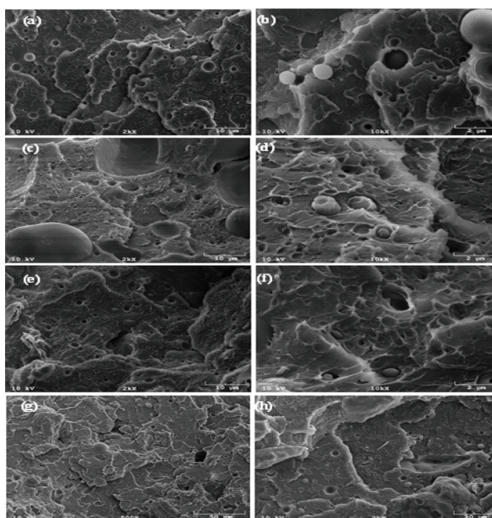


Fig. 4: SEM pictures of the composites. a,b) pure SMA; c,d) SMA/starch blends; e,f) SMA/AC blends; g,h) SMA/NFC blends.

As seen as the SEM pictures, different particle type in the matrix was found to change the morphologic characterization. It was observed that natural fillers were dispersed within matrix and there were some voids in the composites. It can be said that the voids occurred due to esterification reactions between matrix and particles. In many studies, the changes in mechanical properties were found to be depending of linking between polymer matrix and fillers in composites (Simonsen et al. 1998). FTIR analyses were used to determining the chemical structure of the composites (Fig. 5). The FTIR results showed that chemical structures of the composites were similar and that there were no major changes among the composites.

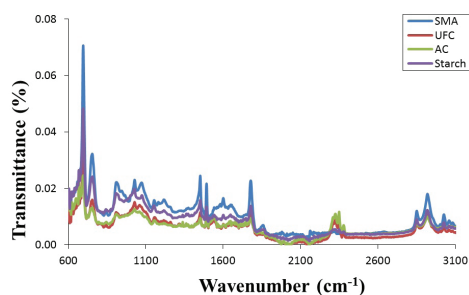


Fig. 5: FTIR Analysis of natural fillers reinforced SMA composites.

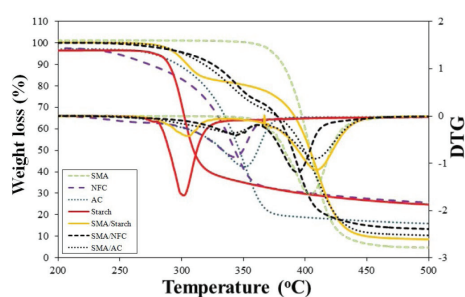


Fig. 6: TGA and DTG analysis of natural fillers reinforced SMA composites.

Thermal stability of the samples was investigated with helping TGA/DTG analysis (Fig. 6). As seen as Fig. 6, adding of natural fillers was found to be not change thermal stability of the SMA.

Onset temperature of the composites was also determined to decrease with adding the fillers. In a study on microcrystalline cellulose with nylon-6 and poly(ethylene terephthalate)-poly(trimethylene terephthalate) blends, the onset temperature of rapid thermal degradation decreases with increasing MCC loading. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the final ash content monotonically increased (Kiziltas et al. 2011a, b). In another study, thermal properties of cellulose nanofibril (CNFs)-filled polypropylene (PP) composites were investigated and thermal properties of the composites with CNFs was found to be lower than pure PP (Yang et al. 2013).

CONCLUSIONS

Natural fillers reinforced SMA composites were produced with thermal melting mixer. The result showed that natural fillers decreased the flexure and tensile strength but has a positive effect on TMOE and FMOE. It was determined that the maximum TMOE was to SMA/AC samples in all composite. Natural fillers were found to be a negative effect on the impact test. The FTIR results showed that chemical structures of the composites were similar and that there were no major changes among the composites, and thermal degradation onset temperature decreased of SMA composites compared to neat SMA because the thermal stability of cellulose fillers is lower than that of neat SMA.

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