Materials and Design 65 (2015) 204–211

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Thermal and dynamic mechanical properties of grafted kenaf filled poly (vinyl chloride)/ethylene vinyl acetate composites

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ARTICLE INFO

Article history:
Received 29 May 2014
Accepted 10 September 2014
Available online 21 September 2014

Keywords:
Chemical reactions
Thermal analysis
Adhesion
Graft copolymerization
Kenaf

ABSTRACT

The effects of kenaf and poly (methyl methacrylate grafted kenaf on the thermal and dynamic mechanical properties of poly (vinyl chloride), PVC and ethylene vinyl acetate, EVA blends were investigated. The PVC/EVA/kenaf composites were prepared by mixing the grafted and ungrafted kenaf fiber and PVC/EVA blend using HAAKE Rheomixer at a temperature of 150 °C and the rotor speed at 50 rpm for 20 min. The composites were subjected to Differential Scanning Calorimetric (DSC), Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR) and Scanning Electron Microscopy (SEM) studies. The DSC data revealed that the crystallinity of the EVA decreased with the addition of 30% grafted and ungrafted kenaf fibers. TGA and derivative thermogravimetric (DTG) curves displayed an increase in the thermal stability of the composites upon grafting of the fiber. Studies on DMA indicate that the T_g of the PVC and EVA in the PVC/EVA/kenaf composites has been shifted to higher temperature with the addition of the kenaf fiber. The presence of PMMA on the surface of grafted kenaf fiber was further confirmed by the analytical results from FTIR. The morphology of fractured surfaces of the composites, which was examined by a scanning electron microscope, showed the adhesion between the kenaf fiber and the PVC/EVA matrix was improved upon grafting of the kenaf fiber.

1. Introduction

The blending of two or more polymers has become an increasingly important technique for improving the cost performance ratio of commercial plastic in order to reduce the cost of an expensive engineering thermoplastic and also to improve the processibility, product uniformity and scrap reduction. The characteristic of a polymer blend is highly dependent upon the method of preparation where it can be manufactured by melt blending, solution blending or dispersion or latex blending. Commercial blends may be homogenous, phase-separated or a bit of both.

PVC is one of the major thermoplastic materials with an enviable and continuing growth. As a hard thermoplastic, PVC offered many useful outdoor applications such as in the building materials, pipe, plumbing and many other applications. With the addition of elastomer, the PVC can be made softer and more flexible which is suitable in electrical wiring. Besides, it is an efficient way to overcome the migration of low molecular weight plasticizer from the PVC and it can also extend the service life of the PVC. EVA copolymers are widely used as a long-lasting life plasticizer for PVC applications where these copolymers have a higher moduli than standard elastomers and can be easily processed without the need to vulcanize. An investigation of miscibility, fracture behavior, surface properties and mechanical properties of PVC/EVA blends were previously reported [1–3].

Abu-Abdeen and Elamer [4] investigated the mechanical behavior of the blend of acrylonitrile butadiene rubber (NBR) and polyvinyl chloride (PVC). Both the elastic modulus and the tensile strength increased with increasing PVC loadings while the elongation at brake recorded a linear decrease. A study on the influence of fiber content on mechanical of untreated bast fiber reinforced poly(vinyl chloride) (PVC) /thermoplastic polyurethane (TPU) polyblend was carried out by El-Shekeil et al. [5]. Poor fiber/matrix adhesion and interfacial bonding were observed in this composite. However, addition of kenaf had enhanced its thermal stability at the higher temperatures. Abu Bakar et al. [6] reported EFB-filled unplasticized poly(vinyl chloride) (PVC) composites. They found

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http://dx.doi.org/10.1016/j.matdes.2014.09.027
0261-3069/

that the incorporation of EFB slightly enhanced the glass transition temperature but it decreased the thermal stability of the composites. Ratnam et al. [7] investigated the effect of oil palm empty fruit bunch (OPEFB) fiber and poly(methyl acrylate) grafted OPEFB on the thermal and structural properties of PVC/ENR blends. Their studies of dynamic mechanical analysis (DMA) indicate that the T_g of the PVC/ENR composite is shifted to higher temperature with the addition of the OPEFB fiber.

Most polymer blends are immiscible on molecular scales which affect their properties. There are several methods available to chemically modify lignocellulose and polymers. Imparting hydrophobicity to the fiber or hydrophilicity to thermoplastic matrix turned out to be the most appealing methods of chemical alteration. The later approach is been applied to natural fiber plastic biocomposites because of the ease of application, specifically maleated polymer is co-compounded with a base polymer together with wood fiber to form products with improved mechanical and water absorption properties. Various coupling agents such as polymeric isocyanates, silanes, and acid anhydrides have been evaluated and have shown improvements in mechanical properties of the final product. Modification of cellulose by graft copolymerization techniques allows one to chemically change the cellulose chain by introducing polymeric chains that confer different structural characteristics of the initial material, which has led to new cellulosic products with improved or new properties.

There is still a lack of comparative studies in the literature to show the effect of kenaf as reinforcement fillers to existing PVC/EVA commercial blends which are commonly used for automotive industry applications. Nur Fatimah et al. [8] reported the effect of methyl methacrylate grafted kenaf on mechanical properties of polyvinyl chloride/ethylene vinyl acetate composites. The use of kenaf fiber is favored because it is a cheap, effective and efficient method to modify the properties of the base material. Chemical composition, structural parameters and properties of kenaf fiber as compared to some selected natural fibers are shown in Tables 1 and 2.

Thermal analysis and dynamic mechanical analysis play an important role in the field of fabrication and application of the composites which need a better understanding to determine the interfacial characteristic of polymeric systems. Graft copolymerization of polymethyl methacrylate (PMMA) on kenaf fiber will change the thermal stability patent of the fiber. In thermal analysis, thermogravimetry has been used to study the thermal degradation and thermal stability of the composites while differential scanning calorimetry has been used to characterize transitions such as crystallization and melting. In amorphous (PVC) and semi-crystalline (EVA) polymer, the types and the amounts of the amorphous and the crystalline phases are related to linear viscoelastic response during dynamic loading. In the present investigation, the thermal and the viscoelastic behaviors of PMMA grafted kenaf fibers reinforced PVC/EVA composite will be studied.

2. Materials and method

2.1. Materials

Poly (vinyl chloride), PVC with *K*-value 70 was purchased from P.T. Asahimas Chemical, Anyer, Indonesia and the PVC stabilizer, tribasic lead sulfate (TBLS) (TS-100M) were purchased from Lonover Scientific Supplier Ltd., London. Ethylene vinyl acetate, EVA with 15% vinyl acetate content was purchased from Polyolefin Company, Singapore (grade COSMOTHENE EVA H2020). The kenaf fiber, grade V36 (a variety of kenaf species that planted in Malaysia), obtained from National Kenaf and Tobacco Board (Lembaga Tembakau Negara), Kelantan State, was used as reinforced materials. The untreated whole stem (core and bast) of kenaf fiber (length 2–6 mm) was prepared by chopping then flaking and followed by the grinding and sieving process to obtain fiber diameter with the size between 100 and 150 μm, the tensile strength is ranged between 50 and 180 MPa. The fiber received was chopped and flecked. Methyl methacrylate (MMA) was purchased from Fluka Chemie (Buchs, Switzerland). It was purified by passing through a column packed with an activated alumina to remove its inhibitor. The Hydrogen peroxide (H_2O_2) used was obtained from Riedel-de-Hazen (Sleelze, Germany) and ammonium ferrous sulfate (Fe^{2+}) was purchased from BDH (Poole, UK).

2.2. Grafting procedures

The primary aim of grafting of kenaf fiber is to reduce the number of hydroxyl groups and to enhance the cross-linking with the polymer matrix. Addition of PMMA results in a hydrophobic interface. Functional groups such as isocyanates [—N═C═O], maleic anhydride [—(CO)2—O—] and dichlorotriazine [—Cl—], derivatizes the polar hydroxyl group of the fibers to form a covalent bond or hydrogen bond. The chemical bonds formed by this process determine the stability of the composite. These bonds influence physical and mechanical properties of the composites. Covalent bonds are generally formed during the modification of the fibers. The polymer matrix can be tailored by graft copolymerization, which can result in better miscibility and cross-linking at the interface.

The optimum percentage of grafting on the surface of kenaf fiber obtained by using response surface methods (RSM). The detailed procedures were described in the works carried out by Nur Fatimah [10]. The process involved three variable parameters: temperature, the amount of hydrogen peroxide and the period reaction. Besides, the constant parameters are the amount of ammonium ferrous sulfate and the amount of monomer (MMA). This situation chosen as referred to the past researches [11,12] where they found that the amount of monomer and ammonium ferrous sulfate used was reached in the similar range at the optimum of percentage.

The reaction was carried out in the thermoset water bath at desired temperature. 1.000 g of fiber was placed in a 250 mL

Table 1
Properties of natural fibers in comparison with glass fibers [9].

Properties	Fiber type							
	Kenaf	Flax	Hemp	Jute	Ramie	Coir	Sisal	Cotton
Density (g/cm^3)	1.5	1.4	1.48	1.46	1.5	1.25	1.33	1.51
Tensile strength* 10E6 N/m^2	350–600	800–1500	550–900	400–800	500	220	600–700	400
E-modulus (GPa)	40	60–80	70	10–30	44	6	38	12
Specific (E/density)	27	26–46	47	7–21	29	5	29	8
Elongation at failure (%)	2.5–3.5	1.2–1.6	1.6	1.8	2	15–25	2–3	3–10
Moisture absorption (%)	–	7	8	12	12–17	10	11	8–25
Price/kg ($), raw (mat/fabric)	0.33–0.88	−1.5 (2/4)	0.6–1.8 (2/4)	0.35 1.5	1.5–2.5	0.25–0.5	0.6–0.7	1.5–2.2