American Journal of Polymer Science & Engineering
http://www.ivyunion.org/index.php/ajpse/

Research Article

Scrutinization of Poly(ethylene-co-ethyl acrylate)/Poly(methyl acrylate) and Zein-based Nanocomposite

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Abstract

In this study, a blend of poly(ethylene-co-ethyl acrylate) (PEEA) and poly(methyl acrylate) (PMA) was prepared using solution technique. Later the blend was reinforced with 1-5 wt.% zein (corn protein) as filler. Mechanical, thermal and morphological characteristics of PEEA/PMA/Zein nanocomposite were measured using suitable techniques. The analysis of the fractured surfaces by scanning electron microscope showed that the zein was dispersed in the form of elliptical grains. Morphology of PEEA/PMA/Zein nanocomposite illustrated homogeneous granular dispersion with no phase separation due to blend miscibility and compatibility with zein nanoparticles. Tensile strength of PEEA/PMA/Zein 1-5 nanocomposite was increased from 30.1 to 45.8 MPa relative to neat blend (24.7 MPa). Similarly Young's modulus of PEEA/PMA with 5 wt. % zein filler was 31% higher than the neat blend. The dynamic mechanical thermal analysis (DMTA) results depicted shift in tan δ peaks of blend at 187 °C to 219 °C in PEEA/PMA/Zein 5 nanocomposite.

Keywords: Poly(ethylene-co-ethyl acrylate); poly(methyl acrylate); blend; solution route; zein; DMTA

Academic Editor: Taihong Shi, PhD, Sun Yat-sen University, China

Received: November 16, 2015; **Accepted**: March 18, 2016; **Published**: May 13, 2016

Competing Interests: The authors have declared that no competing interests exist.

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1. Introduction

Polymer blending is one way for the reduction of cost and enhancement of the properties of polymeric material. The characteristics of polyacrylate blends have been reported in literature [1, 2]. This class of copolymers contains high-molecular weight polymers (ethylene, an acrylate, and carbon monoxide monomer units) in the polymer backbone. The ethylene gives strength, the acrylate contributes to thermal stability and flexibility, and the carbon monoxide contributes polarity to the polymer backbone. The polarity of carbon monoxide makes the polymer miscible with both polar polymers such as poly(vinyl chloride) (PVC) and nonpolar polymers such as polyethylene [3, 4]. Consequently the solubility behavior of polyalkyl acrylates and poly(alkyl methacrylate)s have been studied and compared [3-5]. The solubility behavior of halogen-containing polymers (poly(alkyl acrylate)s or poly(alkyl methacrylate)s) have also been studied [6, 7]. In comparison to poly(alkyl acrylate)s, the poly(alkyl methacrylate)s were more miscible. For a transitional size of alkyl pendant groups, the strength of inter-polymer interaction was displayed maximum. With increasing size of the pendant group, decrease in strength of interaction was observed in polyepichlorohydrin, poly(epichlorohydrin-co-ethylene oxide), and poly(vinylidene fluoride) blend. The solubility behavior of a series of halogen-comprising polymethacrylates with poly(alkyl methacrylate)s was also explored [8-10]. It was displayed that in comparison to poly(alkyl acrylate)s, functional polymethacrylates were more miscible with poly(alkyl methacrylate)s.

Owing to the renewability of raw material and variety of sources, the protein and starch from vegetable origin are significant for food applications [11]. Corn flour is composed of the endosperm, which is constituted of two main fractions of starch and protein [12]. Corn flour based ready-to eat breakfast cereals belong to a family of products whose textural features depend on the reorganization of their components to thermo-mechanical processing [13]. The model blend system of corn starch and zein has been investigated in the past decades. For better understanding, relationship between the mechanical properties and structure of corn flour-based materials have been studied. Under the thermal and mechanical processes, structural modifications of corn flour components, mainly of corn starch and zein, have been deliberated [14]. The water vapour solubility, permeability, moisture barrier, water uptake properties, and mechanical properties of zein–starch composite films have also been measured [15]. Zein is a corn protein that represents about 80% of the total proteins in corn grains. The protein bodies of these grains comprises of three structurally different types of zein: a-zein, g-zein (which includes b-zein), and d-zein. Films of zein are brittle, and the plasticizing influence of glycerol, oleic acid, and poly(propylene glycol) has been investigated for enhancement of their flexibility [16-18]. Zein is also a prospective material for employment in the production of biodegradable plastic because of its thermoplasticity, hydrophobicity, and impermeability to gases [19]. In this study the morphological, mechanical, and thermal features of blend of poly(ethylene-co-ethyl acrylate) (PEEA)/poly (methyl acrylate) (PMA) with different proportions of zein were observed using various techniques.

2. Experimental

2.1 Materials

Poly(ethylene-co-ethyl acrylate) (PEEA, ethyl acrylate 18 wt. %, beads, melt index 20 g/10 min), poly(methyl acrylate) solution (PMA, average Mw ~40,000 by GPC), corn zein protein (powder), and tetrahydrofuran (THF, 99 %) were purchased from Aldrich.

2.2 Instrumentation

The scanning electron microscopic (SEM) images were obtained by Scanning Electron Microscope S-4700 (Japan Hitachi Co. Ltd.). Tensile behavior was examined using a universal testing machine (Instron 4466) with a strain rate of 2 mm/min at 25 ℃ according to ASTM D638 standard method. Dynamic mechanical thermal analysis (DMTA) was performed using a dynamic mechanical thermal analyzer MK III (NJ, USA).

2.3 Poly(ethylene-co-ethyl acrylate)/poly(methyl acrylate) blend preparation (PEEA/PMA)

Binary blend of PEEA/PMA in 1:1 weight ratio was prepared by solution casting using THF at room temperature. Solvent was allowed to evaporate at 40 ℃ for 48 h. The blend was further dried in a vacuum oven at 80 ℃ for 48 h (Fig. 1).

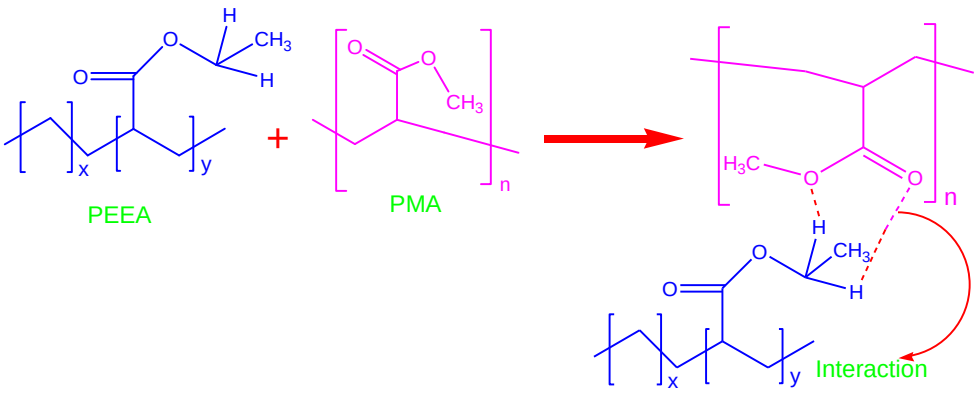

Fig. 1 PEEA/PMA blend formation.

2.4 Nanocomposite preparation (PEEA/PMA/Zein)

Binary blend of PEEA/PMA in 1:1 weight ratio was dissolved in THF with stirring of 6h. Afterwards zein in the desired proportion (1-5 wt.%) was mixed with the blend. The mixture was allowed to stir for further 6h. The mixture was poured in glass Petri dish and solvent was evaporated at 40 ℃ for 48 h. The blend was further dried in a vacuum oven at 80 ℃ for 48 h (Fig. 2).

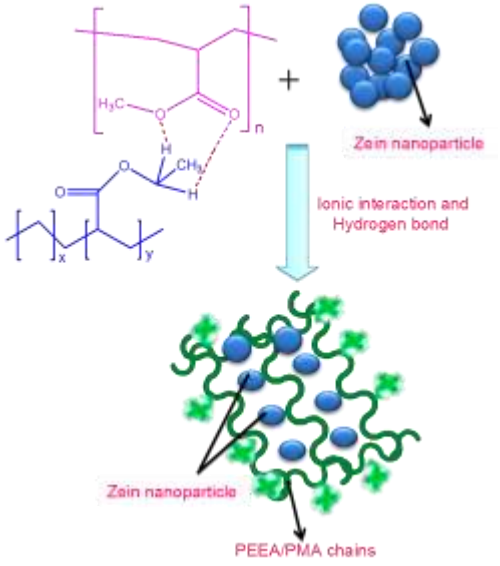

Fig. 2 Interaction in PEEA/PMA and zein composite.

3. Results and Discussion

3.1 Morphology study

Fig. 3 shows the fractured surfaces of PEEA/PMA/Zein 1 and PEEA/PMA/Zein 5 nanocomposites. PEEA/PMA blend with zein particles showed exclusive granular morphology. No separate or distinct phases for blend and zein particles were seen evidencing that the polymers were miscible and nanofiller was compatible with the matrix. With increasing zein content, there was slight increase in the size of accumulated particles. This affect can be observed for PEEA/PMA/Zein 5 with 5 wt. % filler loading (Fig. 3B). These elliptical or oval shaped granular particles were formed because of the coating of PEEA/PMA over zein filler surface. The consistent morphology was due to interfacial bonding that intern influenced the mechanical properties of PEEA/PMA/Zein nanocomposites compared with neat blend [20].

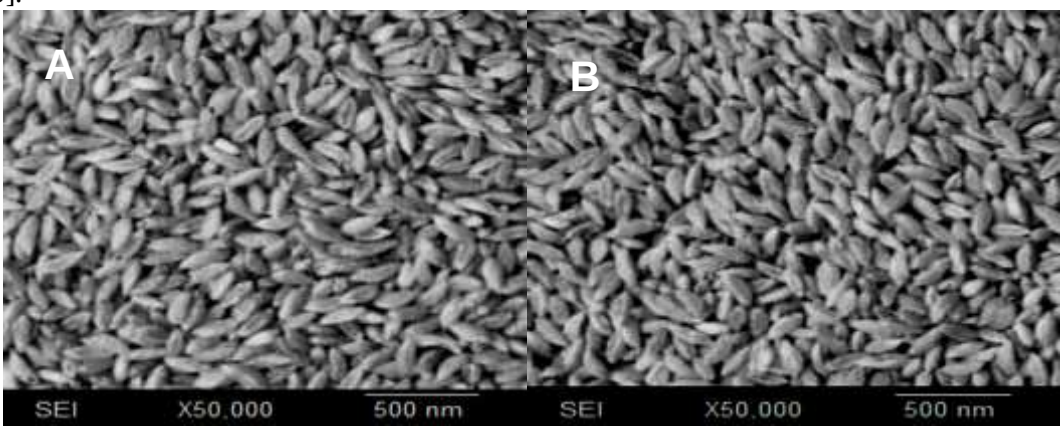

Fig. 3 SEM micrographs of (A) PEEA/PMA/Zein 1; and (B) PEEA/PMA/Zein 5.

3.2. Mechanical properties

Mechanical properties of novel nanocomposites are reported in Table 1. Fig. 4 shows the representative tensile strength curve obtained for PEEA/PMA/Zein 1-5 nanocomposite with varying filler content. The tensile strength of neat PEEA/PMA blend (24.7 MPa) was found to increase with filler loading. The PEEA/PMA/Zein 1-5 nanocomposite showed increase in tensile strength from 30.1 to 45.8 MPa. The Young's modulus for PEEA/PMA/Zein 1-5 nanocomposite was also increased from 199 to 422 MPa with filler addition. Consequently, Young's modulus for PEEA/PMA/Zein 5 was 31% higher than neat blend. However the neat blend showed lower tensile modulus of 130 MPa. Fig. 5 shows the tensile strain curve obtained for PEEA/PMA/Zein 1-5 composite with zein loading. The elongation at break showed decreasing behavior compared with neat blend (15.8 %). The PEEA/PMA/Zein 5 blend indicated that the elongation of break of these blends was strongly reduced by the addition of zein (2.87%). These results suggested that zein had a greater influence on the mechanical properties of PEEA/PMA blends [21].

Table 1 Mechanical properties of PEEA/PMA/Zein composite.

Composition	Tensile Strength (MPa)	Strain (%)	Young's Modulus (MPa)
PEEA/PMA	24.7	15.8	130
PEEA/PMA/Zein 1	30.1	7.11	199
PEEA/PMA/Zein 2	32.9	5.09	333
PEEA/PMA/Zein 3	39.3	3.97	398
PEEA/PMA/Zein 5	45.8	2.87	422

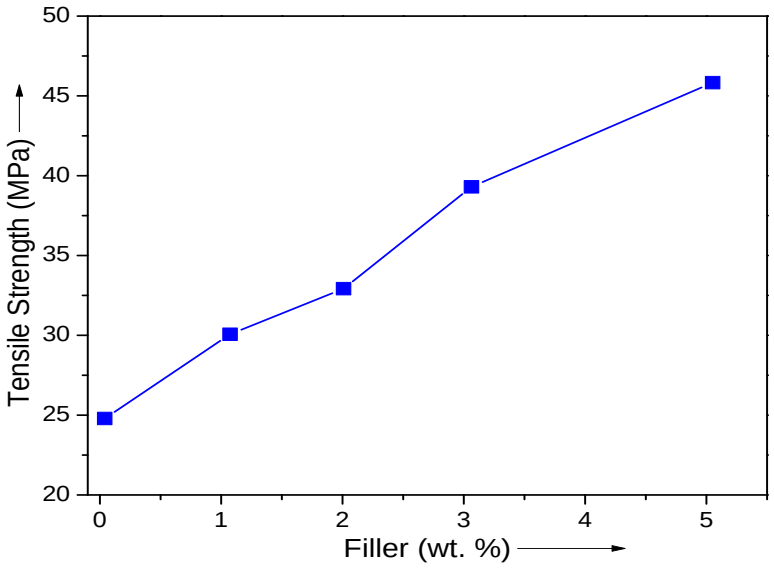

Fig. 4 Tensile strength of PEEA/PMA blend with zein loading.

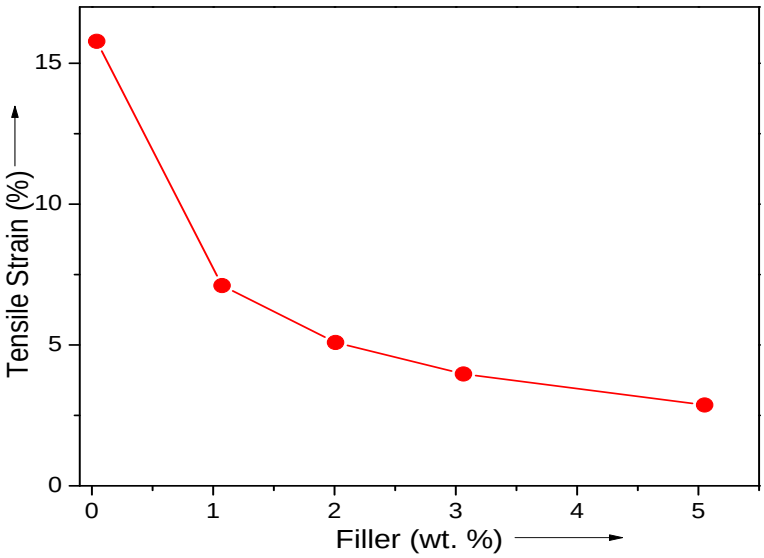

Fig. 5 Tensile strain of PEEA/PMA blend with zein loading.

3.3 Dynamic mechanical thermal analysis

The dynamic mechanical thermal analysis was used to find out the glass transition temperature (T_g) of the PEEA/PMA blend and PEEA/PMA/Zein nanocomposites. The results are shown in Fig. 6. Single peak was observed for the materials indicating blend miscibility and afterwards its compatibility with zein nanoparticles. The tan δ peak for neat blend appeared at 187 °C. The T_g value of PEEA/PMA/Zein 1 was found to increase to 199 °C by peak shift. The tan δ peaks for PEEA/PMA/Zein 2 and 3 were observed at 205 and 211 °C. The highest shift was observed for tan δ peak of PEEA/PMA/Zein 5 to 219 ℃. All peaks were well defined and glass transition was easily located from the graph.

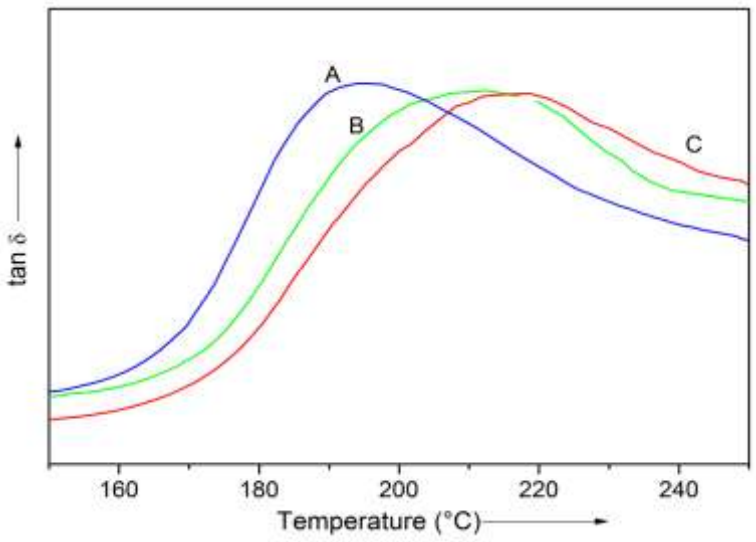

Fig. 6 Plots of tanδ vs. temperature for (A) PEEA/PMA blend; (B) PEEA/PMA/Zein 1; and (C) PEEA/PMA/Zein 5 nanocomposite.

4. Conclusions

The PEEA/PMA/Zein nanocomposite was prepared using facile route. The micrographs depicted miscibility of PEEA/PMA blend and its compatibility with zein nanoparticles. Morphological analysis revealed good dispersion and interfacial adhesion between blend and zein particles. The tensile studies demonstrated several fold improvement in properties over neat blend. The miscible polymer phases seemed to be responsible for the enhanced physical properties. The tan δ peak for neat blend was shifted considerably depicting increase in T_g of blend with filler loading.

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