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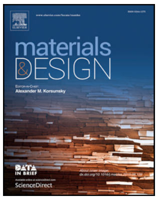


New ternary PLA/organoclay-hydrogel nanocomposites: Design, preparation and study on thermal, combustion and mechanical properties

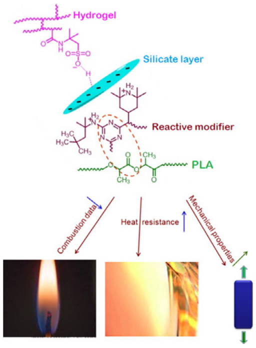
Meisam Shabanian [a],*, Mohsen Hajibeygi [b], Kambiz Hedayati [c], Mahroo Khaleghi [a], Hossein Ali Khonakdar [d]

[a] Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), Karaj, P.O. Box 31745-139, Iran
[b] Faculty of Chemistry, Kharazmi University, 15719-14911 Tehran, Iran
[c] Department of Science, Arak University of Technology, Arak, Iran
[d] Department of Polymer Engineering, Faculty of Engineering, South Tehran Branch, Islamic Azad University, P.O. Box 19585-466, Tehran, Iran

HIGHLIGHTS

- A hydrogel was synthesized and characterized as a new additive for improving PLA properties.
- The hydrogel was added in PLA matrix with and without a reactive organoclay.
- The combination of three components had better properties as compared with the other systems.
- The improved thermal, combustion and mechanical properties were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

A new ternary nanocomposite system containing polylactic acid, an organoclay and a hydrogel was designed and prepared by solution casting method. The hydrogel was synthesized from 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and *N,N′*-methylenebisacrylamide (MBA) via a radical polymerization in the presence of ammonium persulfate (APS). As a potential reinforcement, the hydrogel was used in a PLA system combined with and without a new organoclay. The organoclay was prepared from Cloisite Na^+ and protonated form of SABO®STAB UV 94 via an ion-exchange reaction. The morphology, mechanical, thermal and combustion properties of all the PLA systems were studied. In the presence of the organoclay, the hydrogel showed a synergistic effect on improving all the investigated properties of PLA. The temperature at 5 mass% loss (T_5) was increased from 308 °C to 325 °C in PLA/hydrogel-organoclay nanocomposite containing 3 mass% of each the hydrogel and organoclay (PSH 6) as compared to the neat PLA. The peak heat release rate was decreased from 567.3 W/g for PLA to 410.1 W/g for PSH 6. According to the mechanical tests results, as compared with the neat PLA, by adding both of the hydrogel and organoclay into PLA matrix, the tensile strength was increased from 43.7 to 64.4 MPa.

1. Introduction

Polylactic acid (PLA) is one of the biodegradable polymers derived from renewable sources. As a sustainable replacement for traditional

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* Corresponding author.
E-mail address: m.shabanian@standard.ac.ir (M. Shabanian).

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petrochemical-derived, PLA has attracted much attention in recent years due to its acceptable mechanical, physical properties and high transparency [1]. PLA is developed in packaging applications such as cups, bottles, films and also was used in paper coating, fibers and controlled-release matrices for pesticides, fertilizers and herbicides [2,3]. Due to intrinsic chemical composition and molecular structure, the main problems in PLA are its low thermal stability, melt dripping and high combustibility that led to significantly restrict its new applications in some area such as engineering plastics and flexible electronics. Therefore, good flame retardancy and high thermal stability are important requirements for PLA [4]. However, these problems can be solved or reduced by introducing flame retardant additives, such as montmorillonites as layered materials [5], phosphorus compounds [6], silicon-containing materials [7], carbon-containing materials [8], inorganic materials [9] and flame retardant additives with synergistic effects [10,11]. Similarly, new plasticizers, blending with other polymers, co-extrusion, *co*-polymerization and lamination with more flexible and higher barrier polymers, coating and the formation of new structures with the addition of fillers ranging from non-biodegradable to biodegradable polymers have all been used to improve the properties of PLA-based materials [12].

Among the nanofillers, montmorillonite (MMT), as a kind of clay, has been shown to improve the properties of polymeric materials, by development of polymer/clay nanocomposites (PCN) [13]. These improvements can include high modulus, increased tensile strength and thermal stability and decreased gas permeability and flammability [14]. Considering the flame retardancy, addition of a few of clay (usually <5 mass%) into polymer can remarkably decrease the peak heat release rate of polymers, as long as intercalative or exfoliated structure occurred [15]. Moreover, synergistic effects have been observed when the clay was combined with other flame retardants, such as intumescent flame retardants and inorganic systems [16,17], which can be attributed to the physical and chemical interaction between clay and the flame retardants [18,19].

In general, the conflict between organophilic polymer and the hydrophilic layered silicates has been resolved via surface modification of the nanoclays. [20,21]. Aiming to form strong interaction between the polymer matrix and nanoclay, MMT was generally modified or functionalized with organic compound. Indeed, organo-modification of MMT is very important for the nanocomposites because the interaction between polymer matrix and nanoclay significantly would influence the comprehensive properties of polymer nanocomposites. Some investigation by using different organic modifiers showed that the surfactant structure affected the morphology and properties of the corresponding nanocomposites [22–27]. However, most conventional modifiers of clay are flammable with low thermal stability. The flammability of these materials will eventually limit the fire retardancy of polymer nanocomposites. Therefore, modifiers with low flammability and high thermal stability would be very important for developing high performance clay based polymer nanocomposites.

Hydrogels are cross linked polymer network structures composed of functional hydrophilic groups which have the ability to absorb remarkable amount of water molecules and solute structures [28]. Hydrogels can be prepared from natural and synthetic polymers. Synthetic hydrogel polymers usually have well-defined structures that can be modified to yield tailor able degradability and functionality. Hydrogels can be synthesized from purely synthetic vinyl components. Also, they are stable in the conditions of sharp and strong temperature fluctuations [29, 30].

Hydrogels with three-dimensional polymer networks and large amounts of water, are very interesting due to their unique biocompatibility, flexible methods of synthesis, range of constituents and desirable physical characteristics, good strength and elasticity and widely using in different fields [31,32]. In presence of small-scale inorganic nanoparticles as reinforcing agents the properties of hydrogel were improved [33,34].

Combination of their excellent physical properties with the water-absorbing properties and unique structures of hydrogels, can make them, very good reinforcing materials for improving thermal, flammability and mechanical properties of conventional polymer to achieve high-performance and multifunctional polymer/blend nanocomposites.

PLA and hydrophilic compounds such as starch and hydrogel showed poor compatibility. However, the immiscibility between hydrophilic compound and hydrophobic PLA giving phase separated blend with poor interfacial properties, which could be decrease their compatibility. Hydrophilic compound could mix with the clay and show better miscibility to improve PLA properties [35].

The purpose of this research was to test a new compound for improving the combustion, thermal and mechanical properties of PLA by combining hydrogel and nanotechnology. New PLA/organoclay-hydrogel nanocomposites were prepared using the synthesized hydrogel (Hyd) and a new reactive organoclay (OC) by solvent casting method. The effects of organoclay as a reinforcing agent and a compatibilizer for PLA/hydrogel blend were investigated. Addition of organoclay can improved the dispersion of hydrogel as hydrophilic compound within the PLA matrix.

The modified organoclay with the reactive polymer can act as a compatible compound between hydrophilic hydrogel and hydrophobic PLA. In other hand, due to presence of amide and sulfone groups in the hydrogel structure, the hydrogel can be a good flame retardant and heat insulation for protecting of PLA. Also, the presence of methyl groups in the hydrogel structure can improve its miscibility in the PLA matrix.

2. Experimental

2.1. Materials

PLA type 4042D was provided by Nature works (America). *N*,*N*-dimethyl formamide (DMF), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), *N*,*N′*-methylene bisacrylamide (MBA) and ammonium persulfate (APS) were purchased from Merck and used without further treatment. SABO®STAB UV 94 (Poly[[6-[(1,1,3,3,-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl) imino]-1,6-hexanediyl[2,2,6,6-tetramethyl-4-piperidinyl)imino]])) was purchased from Vanderbilt chemicals company. Cloisite Na^+ (MMT-Na) was purchased from Southern Clay Products.

2.2. Synthesis of hydrogel (Hyd)

A network structure hydrogel based on 2-acrylamido-2-methylpropanesulfonic acid was synthesized via free-radical polymerization according to the following procedure:

3 g AMPS was dissolved in 15 mL distilled water at room temperature. Afterward 0.03 g MBA as cross-linker was added to AMPS solution and the mixture was stirred at room temperature for 30 min. 1 mL solution of APS in water (30 mass%) was added to the mixture and polymerization was completed in water bath at 80 °C after 20 min. The resulting hydrogel was dried in an air-circulating oven at 70 °C for 24 h and finally was crushed into a fine powder. The synthesized hydrogel was then washed in 1000 mL of distilled water for 72 h, changing the distilled water every 24 h for five days. This was done to ensure that any unreacted monomer, initiator or crosslinker was removed.

2.3. Preparation of organoclay (OC)

The surface modification of montmorillonite was carried out by a cation exchange reaction between MMT-Na^+ and an ammonium salt of SABO®STAB to yield organoclay. 5 g MMT-Na^+ was suspended in 700 mL distilled water at room temperature and stirred overnight. In another flask, 2 g of SABO®STAB was dissolved in 60 mL distilled water under magnetic stirring at 60 °C and the pH was adjusted to 3–4 using 1.0 M HCl aqueous solution. After the mixture was stirred for