Polymer Degradation and Stability 96 (2011) 1927–1933

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Effect of fire retardant on flammability of acrylamide and 2-acrylamido-2-methylpropane sodium sulfonate copolymer composites

Nispa Seetapan [a,1], Nattawut Limparyoon [b,2], Suda Kiatkamjornwong [c,*]

[a] National Metal and Materials Technology Center, 114 Thailand Science Park, Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand
[b] Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[c] Department of Printing and Imaging Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 9 April 2011
Received in revised form
1 June 2011
Accepted 22 June 2011
Available online 29 June 2011

Keywords:
Superabsorbent
Zinc borate
Melamine
Fire retardant
Cone calorimetry

ABSTRACT

Poly[acrylamide-*co*-(2-acrylamido-2-methylpropane sodium sulfonate)] superabsorbents and superabsorbent composites (SAPCs) with zinc borate and/or melamine as fire retardants were synthesized. Water absorbencies decreased inversely to added amount of fire retardant. Thermal stability of SAPC/zinc borate increases with increasing zinc borate. Incorporating melamine improved thermal stability of the SAPC until 300 °C. Flammability analysis demonstrated that wood surface coated with SAP or SAPC emulsions extended time to ignition of the wood. Peak heat release rate and total heat release are smallest in specimens coated with SAPC/30% melamine. Wood coated with SAPC incorporating 20% zinc borate/10% melamine mixture gave the longest time to ignition at 4½ min.

1. Introduction

Superabsorbent polymers (SAPs) are lightly crosslinked hydrophilic polymers that can absorb and retain water, saline solutions, or physiological fluids up to thousands times their dry weight. Several ionic vinyl monomers have been copolymerized with a nonionic hydrophilic monomer to prepare SAPs with high degree of swelling [1–7]. Based on the superior water swellable characteristic, SAPs have been widely used in the fields of personal care products [8], agricultural soil [9], wastewater treatment [5,6,10–14], as well as in fire-fighting application [15–17]. In the later case, water is typically used to extinguish the fire or to prevent combustible objects from burning by reducing the temperature of the combustible material below the burning temperature. However, when a fire is extinguished by spraying water onto it, only a small amount of the total water applied is generally effective in extinguishing the fire, due to loss of most of the water, such as by run-off or evaporation of the water. Therefore, SAPs have been proposed as a method to prolong a combustible object from burning, or to prevent the penetration of extreme heat or fire to a combustible material. To prevent the spreading of fire, a sufficient amount of swollen SAPs have to be sprayed onto an ignitable or burnable object so as to continuously coat the surface of the object nearby the burning fire. Here, the mechanism of preventing the fire spreading is to both cool the surface of the object below the ignition temperature and to reduce the quantity of oxygen at the surface of the burnable object to a degree such that the flame is extinguished [16]. However, SAPs are organic materials which lose their thermal stability when exposed to high temperatures. Therefore, for fire-fighting applications, the incorporation of a fire retardant into SAPs can offer thermal protection from fire due to the ability to absorb high amount of water together with the thermal stability provided by the added inorganic materials. However, unlike the extensive studies on improving fire-retardant property of thermoplastics, thermosets, elastomer, and wood [18–22], the investigation of SAPs with thermal stability and fire-retardant properties for fire-fighting applications is rather limited [23,24]. Our previously published results on flammability analysis using cone calorimetry technique revealed that the wood specimens coated with SAP or SAP/mica nanocomposite showed an excellent reduction in the peak heat release rate, and extended the time at peak heat release rate, but did not reduce the total heat release [24].

Among several characterized fire retardants, zinc borate has been found to be an effective inorganic fire retardant that possesses

* Corresponding author. Tel.: +66 2218 5587; fax: +66 2255 3021.
E-mail addresses: nispam@mtec.or.th (N. Seetapan), winny047@hotmail.com (N. Limparyoon), ksuda@chula.ac.th (S. Kiatkamjornwong).
[1] Tel.: +662 564 6500.
[2] Tel.: +662 594 1344.

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.06.014

key characteristic properties of flame retardants, such as smoke suppression and promoting charring, and so on [25], that are required by new fire standards. It has been postulated that the mechanism of the zinc borate induced flame retardancy in polymeric materials involves the formation of a protective char layer at surface of the materials, which then obstructs the access of oxygen and subsequently prevents the oxidation of carbon [26]. As such, zinc borate is commonly used as a multifunctional flame retardant in combination with other halogenated or halogenated free flame retardant systems to boost flame retardancy properties [27]. Melamine is another type of nitrogen-containing flame retardants and has been used in thermoplastics [28,29]. The mechanism of melamine's fire retardancy has been reviewed and is proposed to be due to the sublimation and vapor-phase dissociation, where it is converted to non-volatile products and ammonia [30]. Therefore, in this study, we have incorporated different loadings of zinc borate and melamine into the synthesis of acrylamide (AM) and 2-acrylamido-2-methylpropane sodium sulfonate (AMPS-Na^+) SAPs. These potential fire retardants of the obtained superabsorbent composites (SAPCs) were evaluated for their water absorbency, thermal stability and flammability. AMPS-Na^+ was chosen because its strongly ionizable sulfonate groups can provide SAPs with a high water swelling capability. The novel fire retardant incorporating SAPCs that showed the best tap-water swelling, thermal stability and flammability might be appropriate for inhibiting the spreading of fire.

2. Experimental

2.1. Materials

Acrylamide (AM) was gifted from Siam Chemical Industry Co., Ltd. (Bangkok, Thailand). 2-acrylamido-2-methylpropane sodium sulfonate (AMPS-Na^+) was purchased from Aldrich (Steinhiem, Germany). *N,N′*-methylenebisacrylamide (MBA) and *N,N,N′,N′*-tetramethylethylenediamine (TEMED) were received from Fluka (Buchs, Switzerland). Ammonium persulfate (APS) was from Ajax (Seven Hills, Australia). Zinc borate ($2ZnO_2B_2O_3 \cdot 3H_2O$, Aldrich, Steinhiem, Germany) and melamine ($C_3H_6N_6$, Thai Mitsui Specialty Chemicals Co., Ltd., Chachoengsao, Thailand) were employed as fire retardants. Deionized water (Elga Deionizer, Model LA611, U.K.) was used for the synthesis and the swelling experiment.

2.2. Preparation of AM-co-AMPS-Na^+ SAPs

SAPs were synthesized by free-radical crosslinking polymerization of AM and AMPS-Na^+ at the molar ratio of 15:85, with 0.05% mol of MBA (crosslinker). An equal concentration of APS (initiator) and TEMED (co-initiator) was used at 1.2% by mol of the monomers. These concentrations were selected as being found previously to yield the SAP with the highest water absorbencies [24]. Firstly, AM was dissolved in deionized water in a 500-cm^3 reactor equipped with a mechanical stirrer, a condenser, and an inlet tube of nitrogen gas. AMPS-Na^+ was then added and the mixture was stirred at room temperature for 5 min, before heating to 60 °C under nitrogen atmosphere. Next, MBA and APS were sequentially added to the mixture and stirred for 5 min. Finally, TEMED was added and the polymerization was proceeded for 30 min to ensure complete polymerization. The obtained product was dehydrated with acetone, dried, milled, and then sieved through a 100-mesh sieve aluminum screen.

SAPs/fire retardant composites were synthesized by incorporating the desired amount of fire retardant into the polymerization mixture before MBA, APS, and TEMED were added. In this study, zinc borate, melamine, and their mixtures were chosen as fire retardant systems.

2.3. Fourier transform infrared spectroscopy (FT-IR)

The existence of the components of each SAP or SAPC was evaluated by analysis of their respective functional groups by Fourier Transform Infrared Spectroscopy (FTIR; System 2000, Perkin Elmer, U.S.A.). The dried sample and KBr powder were mixed, ground, pressed, and then subjected to the FT-IR spectrometry.

2.4. Water absorbency measurement

The water absorbency of the SAP and its derived SAPCs containing zinc borate, melamine or both, was carried out at room temperature. Each 0.1 g aliquot of dried SAP or SAPC product was allowed to swell in 200 cm^3 of deionized or tap water for 24 h. Subsequently, the fully swollen superabsorbents were separated from the unabsorbed medium by filtering through a 100-mesh sieve aluminum screen for 2 h. The swollen superabsorbents were then weighed and the water absorbency at equilibrium ($g\,g^{-1}$) was calculated by Eq. (1) and they were performed in triplicate for each system:

$$\text{Water absorbency} = \frac{\text{weight of swollen gel} - \text{weight of dry gel}}{\text{weight of dry gel}} \tag{1}$$

2.5. Thermal stability analysis

The SAP and its derived SAPCs were investigated for thermal properties using a TGA/SDTA 851e (Mettler Toledo Corporation, Switzerland). The measurements were carried out over a temperature range of 25–800 °C at a heating rate of 10 °C min^{-1} with a nitrogen gas flow rate of 60 $cm^3\,min^{-1}$.

2.6. Flammability test

Flammability analysis was evaluated using a cone calorimeter (Fire Testing Technology Ltd., UK), according to ISO 5660, at an incident heat flux (50 $kW\,m^{-2}$) in an air atmosphere, and under the free convective air flow condition. The SAPs were prepared in the form of an oil-in-water dispersion as follows [31].

The dry SAPs or SAPCs (40% $w\,w^{-1}$) were dispersed in a mixture of 50% $w\,w^{-1}$ of palm oil and 10% $w\,w^{-1}$ of nonionic surfactant blends containing 54% $w\,w^{-1}$ of Tween 80 or poly(oxyethylenesorbitan monooleate) having the HLB of 15 and 46% $w\,w^{-1}$ of Span 80 or sorbitan (Z)-mono-9-octadecenoate having the HLB of 4.3 to give the HLB value of the blend is 10. Each suspension (5% $v\,v^{-1}$) in the oil-surfactant mixture was then dispersed in tap water, to subsequently obtain a viscous slurry gel that was used as an emulsion to coat wood (Apocynaceae, *Wrightia religiosa* Benth.) board dimension $100 \times 100 \times 3$ mm to a surface depth of 3 mm. The surface of the wood, both uncoated and coated from the same batch, was subsequently exposed directly to an open flame generated by a propane gas jet. The uncoated wood board was used as the relative control to compare the effectiveness of the SAP and SAPC gels as fire retardants. The time to ignition (t_{ign}), peak of heat release rate (PHRR), time to PHRR (t_{PHRR}) and total heat release (THR) were recorded. The charred samples left after the flame extinguished were photographed by a digital camera.

3. Results and discussion

3.1. Synthesis of poly(AM-co-AMPS-Na^+)/fire retardant SAPCs

The IR spectra shown in Fig. 1(a)–(e) of zinc borate alone and that after the nominal incorporation of 5, 10, 20, and 30% $w\,w^{-1}$ into the SAPCs revealed that the zinc borate alone shows peaks as