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Polymer Degradation and Stability 88 (2005) 106–113
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Flame retarded polyurea with microencapsulated ammonium phosphate for textile coating

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Received 15 September 2003; accepted 26 January 2004
Available online 11 November 2004

Abstract

Two types of microcapsules of di-ammonium hydrogen phosphate (DAHP) with respectively polyether-polyurethane shell and polyester-polyurethane shell were evaluated as intumescent flame retardant (FR) in a commercial polyurea coating for textiles. The expected advantages of this new concept of encapsulated FR agent are to be compatible with a polymeric matrix in order to give a permanent FR effect and to be itself an efficient FR intumescent formulation for many materials. The thermal degradation for the two types of DAHP microcapsules shows characteristics of an intumescent formulation. The reaction to fire of cotton fabrics coated by FR polyurea loaded with neat or microencapsulated DAHP was studied with the cone calorimeter as the fire model. Both types of DAHP microcapsule present in the polyurea coatings on cotton fabric give an efficient FR effect, although the char developed with microcapsules is a little less heat resistant than that developed with the pure DAHP. Coatings containing microcapsules with polyester-polyurethane shells evolve the smallest quantity of smoke and CO.

Keywords: Polyurea; Microencapsulation; Phosphate; Intumescence; Thermal degradation; Textile; Coating; Cotton

1. Introduction

Polyurethane/urea (PU) is a unique polymer with a wide range of physical and chemical properties such as abrasion resistance, water repellency, leather appearance, etc. These properties provided by PU coating to cotton or cotton-polyester blended fabrics are very attractive in many textile applications: transportation (e.g. car seats), apparel (e.g. waterproof breathable jackets), and furnishings (e.g. artificial leather upholstery). But these PU coatings have poor flame retardancy.

The addition of a flame retardant to PU coatings is necessary to improve the fire behaviour of the coating and the underlying material. Polyurethane–phosphate combinations are known to form flame retardant (FR) intumescent systems [1–4]. The intumescent formulation is not permanent because of the water solubility and migration of the phosphate. This problem might be

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doi:10.1016/j.polymdegradstab.2004.01.028

solved by the technique of microencapsulation. Microencapsulation [5–7] is a process of enveloping microscopic amounts of matter (solid particles, droplets of liquids or gas bubbles) in a thin film of polymer which forms a solid wall. This core/shell structure allows the isolation of the encapsulated substance from the immediate surroundings and thus protects it from any degrading factors such as water. We have synthesized microcapsules containing di-ammonium hydrogen phosphate (DAHP) with a polyurethane shell [8,9]. It is of interest to study microencapsulation with a polyurethane shell for two main reasons. First, we can expect that microcapsules with PU shells will be compatible with the final PU coating on the textile and also with other polymeric matrices. Secondly, combination of the encapsulated ammonium phosphates and the PU shells should be an intrinsic FR intumescent formulation. Microcapsules are obtained by two different techniques, microencapsulation by interfacial polymerization (IP) [10] and microencapsulation by evaporation of solvent (ES) [11]. In a previous work [12], we demonstrated that the concept of using IP microcapsules of phosphate in a polyurethane coating was efficient in providing flame retardancy for cotton fabrics.

In this paper, the IP microcapsules, the new ES microcapsules and their components (neat DAHP and neat PU shell) are examined by thermal analysis in air. Interactions between DAHP and the two types of PU shell were studied due to thermal gravimetric curves of microcapsules and their components. Cotton fabric was coated by several formulations of polyurea resin with either different loadings of microencapsulated DAHP (IP and ES types) or neat DAHP. The reaction to fire of these different textile coatings (in particular with ES microcapsules) is studied using the cone calorimeter as fire model [13,14].

2. Experimental

2.1. Materials

Raw materials were used without further purification.

The synthesis of IP and ES microcapsules of DAHP (μPI and μES) was described in previous papers [8,9]. The polyurethane shell of IP microcapsules is synthesised from diphenyl methylene diisocyanate (blend of MDI isomers, principally 4,4′-diphenyl methylene diisocyanate), polyethylene glycol with a number average molecular weight of 400 g mol^{-1} (PEG 400) and some water. The polyurethane shell of ES microcapsules is synthesised from pure 4,4′-diphenyl methylene diisocyanate, poly(hexamethylene adipate) glycol with a number average molecular weight of 3800 g mol^{-1} (PHMA 3800) and ethylene diamine (EDA). We characterized the two types of microcapsules [8,9]. Their physicochemical characteristics are summed up in Table 1. While, weight percentages of encapsulated DAHP are certainly low, nevertheless it is interesting to note that PU shell is an efficient barrier to reduce DAHP dissolution in water especially for ES microcapsules. We also synthesised two types of microcapsule with the same PU shells but without DAHP in order to study their thermal behaviour.

Table 1
Physicochemical characteristics of IP and ES microcapsules of DAHP

Measured properties	IP microcapsules	ES microcapsules
Diameter	Number average: 3.35 μm	Between 20 and 100 μm
Chemical characteristics of the shell	Poly(ether/urethane/urea) crosslinked	Poly(ester/urethane/urea) crystallized soft segment
Weight percentage of DAHP	3%	1%
Weight percentage of lost DAHP for microcapsules dispersed in water (7days)	0.09%	0.03%

A pure cotton fabric (146 g m^{-2}) was coated by a commercial polyurea paste from Allrim obtained from a mixture of 20 parts of polyamine (BD021 AW; aromatic diamine) and 100 parts of polyisocyanate (BD021 BY; blend of diphenyl methylene diisocyanate isomers). We incorporated in this paste 20 and 30% (by weight) of solid DAHP, $(NH_4)_2HPO_4$ (purity 99% minimum) from Riedel-de Haën AG, or 20% of DAHP microcapsules (IP or ES types) synthesised in our laboratory.

2.2. TGA experiment

All TGA tests were carried out using TGA 2950 from TA Instruments at a linear heating rate of 10 °C min^{-1} in air (60 ml min^{-1}; Air Alphagaz 1 from Air Liquide). The weight of all samples was kept within 9–10 mg. The temperature range was from ambient to 800 °C. Concerning thermal analysis of IP and ES microcapsules, curves of weight difference between the experimental and theoretical TG curves are computed as follows:

$$\Delta(M(T)) = M_{\mathrm{exp}}(T)_{[\mathrm{microcapsule}]} - M_{\mathrm{theo}}(T)_{[\mathrm{PU\ shell/DAHP}]}$$

where $\Delta(M(T))$ is the curve of residual mass difference, $M_{\mathrm{exp}}(T)_{[\mathrm{microcapsule}]}$ is the experimental residual mass of IP or ES microcapsules (variation by temperature T), $M_{\mathrm{theo}}(T)_{[\mathrm{PU\ shell/DAHP}]}$ is the theoretical residual mass of the same microcapsules computed by linear combination between the experimental residual masses of DAHP and PU shell (IP or ES types):