

Plasma-induced graft-polymerization of flame retardant monomers onto PAN fabrics

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Abstract

This paper presents the use of the low-pressure plasma technique to confer a fire-resistant character to polyacrylonitrile (PAN) textiles. We investigated the argon plasma-induced graft-polymerization of four acrylate monomers containing phosphorus, diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl) phosphonate (DEAMP) and dimethyl(acryloyloxymethyl)phosphonate (DMAMP), which are known to be effective monomers for the fireproofing of polymeric substrates in classical polymerizations. The grafting and the polymerization processes taking place on the surface of the PAN textile were followed by weighing measurements, IR(ATR) spectroscopy and SEM. The fire retardant character of the treated fabrics was investigated by thermogravimetric analyses and LOI measurements. Furthermore, we were able to prove the persistence of the coatings towards several washing cycles by using the accelerated method of laundering proposed by McSherry and al.

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1. Introduction

Polyacrylonitrile fibers are widely used for home textiles (furniture covering, curtain materials, wall hangings, textile wall covering, carpets and stores) as well as knitwear and clothing. These fields of use are increasingly subject to flame proofing regulations, so that there is a need for the improvement of flame retardant finishing of PAN fibers.

Numerous flame proofing agents have been already tested to fire retard PAN fibers/fabrics, and among them phosphorus compounds were found to be suitable for this application [1]. Although their action is still unexplained, it is generally admitted that the flame retardant effect of these compounds is directly related to their char forming tendency

and their ability to reduce the flammable volatiles formed during the first stage of pyrolysis of acrylonitrile polymers. This occurs via the cyclization of the nitrile groups which is initiated by acids like phosphoric acids which are formed during the combustion of fabrics containing phosphorus compounds.

Among all the phosphorus compounds usually employed for this application [1–3], acrylic monomers of the type described in Scheme 1 have shown good fire retardant properties [4].

They can be introduced either as co-monomers (method A) or as additives (method B). In the latter case the polymeric material is employed instead of the monomer (Fig. 1).

Whatever the procedure employed, it was possible to increase the LOI values of the final fabrics of at least 6 units compared to the untreated fabrics. However, to achieve that result, a minimum content of 3% by weight of phosphorus is necessary. Taking the molecular mass of the phosphorus containing monomer or polymer into account, a minimum

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of 25–30% by weight must be added in the classical fabrication processes (A or B). This implies, in the reactive approach (A) a good compatibility between the co-monomers and a homogenous distribution during the polymerization. For the additive approach (B), the polymer should be soluble in the spinning solution, compatible, should not influence the viscosity and of course, for both approaches, the physical and the mechanical properties of the fiber should not be affected. All these restrictions limit considerably the range of the monomers which can be used and overall, the flame proofing effect should be permanent and therefore resistant to several cycles of laundering, which is not the case when they are employed as additives. To overcome all these inconveniences, it is worth considering an alternative procedure (C) (surface approach) where the flame retardant agent is coated and covalently linked onto the surface of the fiber/fabric.

Among all the different kinds of surface treatments (wet or dry), the cold plasma technique is one of the processes allowing to graft covalently small functional groups as well as macromolecular compounds. Furthermore, the modification of the surface is obtained without affecting the bulk properties [5]. There are three different ways to use the cold plasma technique. The first one consists of a simple modification of the surface structure of the material and/or functionalization by using non-polymerizable gases such as N_2 , O_2 , H_2 , NH_3 , CO_2 , etc. In the second method, the plasma is generated with volatile organic, organosilicon or organometallic compounds which lead to the deposition of a thin polymer film on the surface of the material. This is *plasma polymerization*. The third method is the *plasma grafting*. In that case, the plasma is employed only to activate the surface of the material. The grafting step of a polymer for instance is performed afterwards in a separate step in a solution containing the monomer either by heating or by using UV or γ radiations. Note in this context that the simple polymerization of non-volatile monomers by noble gas plasmas has been investigated [6]. It appeared to us that both steps, that is activation of the surface and simultaneous grafting and polymerization of a non-volatile monomer, can be performed in a single work-step in the plasma chamber: this is *plasma-induced graft-polymerization*. Evidently this method is of considerable practical interest.

The fire retardation of polymers and textiles has been achieved using one of the cold plasma procedure outlined above, that is: (i) grafting of phosphorus non-volatile compounds and polymers in a cold plasma [7,8], (ii) deposition of organosilicon compounds by plasma polymer-

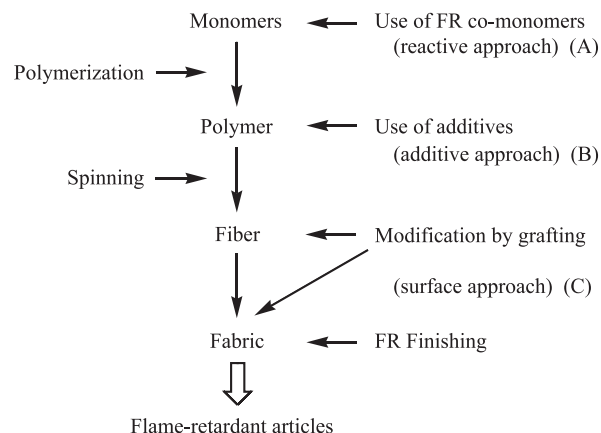


Fig. 1. Flame retardant finishes [1].

ization [9,10] or (iii) by the cold remote nitrogen plasma (CNRP) method recently developed by Jama et al. [11,12], (iv) CF_4/CH_4 plasma deposition [13] and (v) plasma grafting using acrylic monomers developed by Laishun Shi et al. [14,15].

The *plasma-induced graft-polymerization* procedure we have developed in our laboratory [16–18] and applied to PAN fabrics in order to confer to these material new and durable properties is depicted in Fig. 2.

In step (1), the PAN fabric samples (S) were immersed at room temperature in a solution containing the monomer (M), a photoinitiator and eventually a cross-linking agent. After the removal of the excess of the solution, the substrate was submitted in step (2) to the Ar plasma ($P=100$ W; $F_{Ar}=125$ sccm; $p=40$ Pa) for various treatment times. Finally, the sample was washed in step (3) and dried in step (4). Afterwards the grafted polymer was characterized.

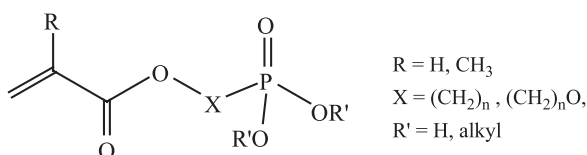
By using this procedure, we tried to induce in one step simultaneously the grafting and the polymerization of various monomers using an Ar plasma. The desired properties are achieved by creating covalent bonds between the PAN fabrics and the growing polymer at the surface.

In this paper we present this methodology to enhance the flame behavior of PAN textiles by using four acrylates monomers containing phosphorus: diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl) phosphonate (DEAMP) and dimethyl(acryloyloxymethyl)phosphonate (DMAMP) (Scheme 2).

2. Experimental

2.1. Materials and reagents

Woven PAN fabrics ($290\text{--}300$ g/m²) were kindly supplied by the Dickson-Constant Society. The syntheses of the following monomers, diethyl(acryloyloxyethyl)phosphate (DEAEP), diethyl-2-(methacryloyloxyethyl)phosphate (DEMEP), diethyl(acryloyloxymethyl) phosphonate (DEAMP) and dime-



Scheme 1. P-containing monomers.

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