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Ultraviolet resistance of azo-containing poly(1,3,4-oxadiazole) fibres

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ABSTRACT

To improve the ultraviolet (UV) resistance of poly(1,3,4-oxadiazole) (POD) fibres, 4,4′-azodibenzoic acid (ADA) was introduced into the POD fibres through copolymerization and blending respectively. The influence of UV light on the intrinsic viscosity and mechanical properties of POD fibres with and without azo groups was investigated in detail. The results revealed that the tensile strength retention of the POD fibres containing ADA was much higher than that of the POD fibres without the azo groups (p-POD) after accelerated irradiation using an iodine-gallium lamp. It was also found that POD with ADA in the molecular chain (c-POD) by copolymerization showed better UV stability than that of the POD blended with the same amount of ADA (b-POD). The UV spectrum was used to explore the UV resistance mechanisms of the series of the POD containing azo groups and it was demonstrated that the mechanisms of b-POD and c-POD were different.

1. Introduction

Aromatic polyoxadiazole (POD) has excellent heat resistance because of its rigid structure and strong covalent bonds. POD is a kind of conjugated polymer with excellent photoelectric properties, which is similar to polythiophene (PTh), poly-p-phenylene benzobisthiazole (PBO) and poly(phenylene vinylene) (PPV). It has been reported [1–4] that most conjugated polymers are sensitive to ultraviolet (UV) light and present weak UV resistance. The conjugated polymers such as PTh, PBO and PPV degrade much faster than the non-conjugated polymers under the same UV conditions. Many researchers [5–7] have done a lot of work to study the thermal properties of POD, but studies on the UV irradiation of POD are relatively few. Imai [8] pointed out that the UV resistance of POD was similar to Nomex fibres. In our previous work [9], the mechanical and structural properties of the POD fibres exposed to UV light were comprehensively studied and the mechanisms of the photo-degradation was proposed. However, methods to improve the UV resistance of POD have been rarely documented and studied. Generally, there are three frequently-used methods to improve the UV resistance of fibres. The coating method covers the fibres or fabrics with UV protecting additives, which usually has the main disadvantage of losing the coating materials slowly over time and thus leads to losing protection finally. The second method is blending the light stabilizers into the fibres. Benzotriazole UV absorbers, hindered amine light stabilizers and many other conventional light stabilizers were used to enhance the UV resistance of conjugated polymers [10]. As the POD generally need to be dissolved in concentrated sulphuric acid or polyphosphoric acid for forming, which will destroy the structure of the light stabilizers, many of those light stabilizers used for POD performed poorly. So the exploration of an effective light stabilizer for POD fibres is imperative. Changing the molecular structure by copolymerisation, as a third method, is also an effective way. The UV absorption of the conjugated structure is the main reason that results in the aging of the polymer, because the energy of the UV light is enough to break the chemical bonds of the polymer. The change of the molecule structure will lead to some change of the absorption of UV light, so the UV resistance will be improved fundamentally. For instance, the UV resistance of POD was partly improved after reducing the conjugation by introducing isophthalic acid into the main chain of POD [11]. However, most of the co-monomers will be destroyed in the polymerization conditions of POD.

Aromatic azo compounds have already been used for polydienes and the activity mechanisms of those compounds were also investigated [12]. It is thought that the azo compounds may act as the light absorbers because of their photochemical isomerisation and they may also act as antioxidants when attached with some specific terminal groups. It is interesting to attempt to use aromatic azo compounds to improve the UV resistance of POD, moreover, the study of using methods also seems significant. In the present work, 4,4′-azodibenzoic acid (ADA) with two reactive carboxyl groups

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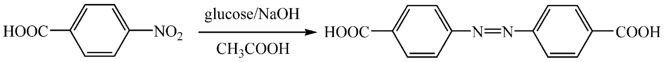


Scheme 1. The synthesis of ADA.

was synthesized and introduced into the POD fibres by blending (b-POD) and copolymerization (c-POD) methods, respectively. The UV resistance of b-POD and c-POD fibres was investigated through accelerated UV aging. The mechanical and thermal properties of POD fibres exposed to UV light were studied, and the UV resistance mechanisms of b-POD and c-POD are also discussed.

2. Experimental

2.1. Materials

4-nitrobenzoic acid, glucose, sodium hydroxide, concentrated hydrochloric acid, ammonia water, terephthalic acid, hydrazine sulphate, fuming sulphuric acid (20% SO_3), benzoic acid (all from Ke Long Co., Ltd., Chengdu, China), glacial acetic acid (from Chang lian, Chengdu, China) were analytically pure and used as received.

2.2. Synthesis of 4,4′-azodibenzoic acid (ADA)

ADA was synthesized according to the method described by Ghosh et al. [13–15], as is shown in Scheme 1.

^1H NMR (DMSO-d_6, 600 MHz): δ 8.16 (d, 4H), δ 8.01 (d, 4H) ppm. FTIR: the peak at 1685.9 cm^{-1} was the stretching vibration of the C=O, the broad peak from 2962 cm^{-1} to 2542 cm^{-1} was the stretching vibration of the O–H, and the peak of N=N was appeared at 1423.3 cm^{-1}.

2.3. Preparation of POD fibres

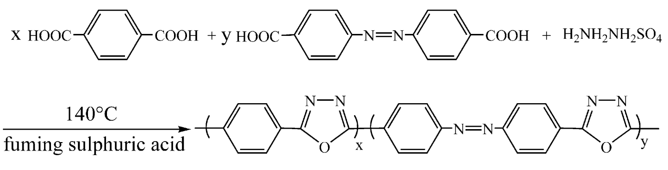
2.3.1. Preparation of p-POD and c-POD fibres

POD was synthesized by one step with three stages and its fibres were prepared by wet spinning as was described in our previous work [16,17]. Scheme 2 shows the synthesis route of p-POD and c-POD. A series of c-POD fibres were obtained by changing the content of ADA. The series of c-POD are marked as y-c-POD in this paper (y is the molar percentage of ADA of the total diacid). The p-POD was obtained when the copolymerization was taken without ADA.

2.3.2. Preparation of b-POD fibres

The b-POD fibres were acquired by blending ADA into the spinning solutions of p-POD homogeneously and ADA existed as molecular state in the solutions finally. The series of b-POD are marked as y-b-POD (y is the molar percentage of ADA of the total diacid).

The colour of the p-POD fibres is faint yellow, while the b-POD and c-POD fibres are red. In addition, the colour of the b-POD and c-POD will darken when the used amount of ADA increases. The linear density of all the obtained fibres is almost the same.



Scheme 2. The synthesis of p-POD and c-POD.

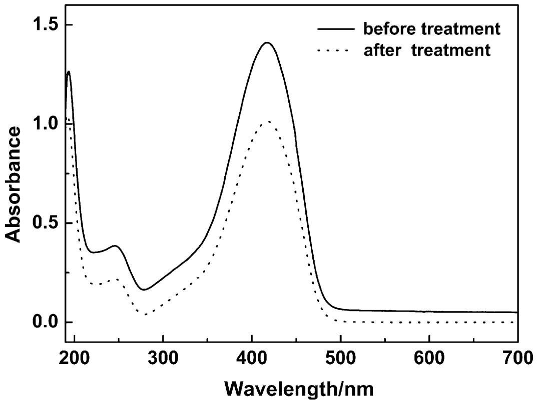


Fig. 1. The UV–vis spectra of ADA before and after treatment in concentrated sulphuric acid at 140 °C.

2.4. The accelerated irradiation of the prepared fibres

All of the POD fibres were irradiated by an iodine–gallium lamp, whose emission wavelength was 200–450 nm. The irradiation power of the lamp was 800 W/m^2 and the distance between sample and lamp was 35 cm. The UV aging tests were conducted under 30 ± 0.5 °C. The aged samples at different duration of exposure to UV light were collected for mechanical tests.

2.5. Experimental techniques

The intrinsic viscosities ($[\eta]$) of polymer samples were determined with an Ubbelohde viscometer ($D_1 = 0.9–1.0$ mm) using 98% sulphuric acid as solvent at 30 ± 0.1 °C, with polymer concentrations ranging from 0.20 to 0.40 g/dL. Intrinsic viscosities were determined by the usual double extrapolation of η_{sp}/C and $(\ln \eta_{rel})/C$ to zero concentration. The plots obtained were linear in all cases.

Mechanical properties were measured using the YG001A-1Model tensile tester with a 10 cN load cell. Tests were conducted on single fibre specimens using a crosshead velocity of 20 mm/min and a gauge length of 20 mm. All the tensile tests were carried out at the constant temperature of 25 °C and relative humidity of 70%. Twenty single fibre specimens were measured to take the average.

Thermogravimetric analysis (TGA) was carried on a TA Instruments Q600. The fibre samples were cut into powder and dried in a vacuum oven for 12 h. The measured temperature was varied from 150 °C to 600 °C at a heating rate of 10 °C/min under nitrogen.

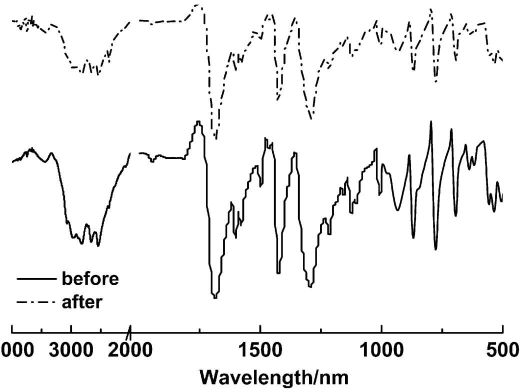


Fig. 2. The FTIR spectra of ADA before and after treatment in concentrated sulphuric acid at 140 °C.