Improvement of Dyeability of Para-Aramid Fibers Using Electron-Beam-Induced Graft Polymerization

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Abstract: The surface modification of a para-aramid fiber was investigated by graft polymerization of a vinyl monomer having an anionic group onto radicals on the fiber surface that were induced by electron beam (EB) irradiation. Generation of the radicals in the fiber irradiated with EB was evaluated, and it was determined that the radical concentration of the fibers increased with an increase in the dose of radiation. Acrylic acid (AA) was used as the anionic vinyl monomer for graft polymerization. Dyeability was improved for the fabrics that had been graft polymerized with AA because of the formation of ionic bonds between the anionic groups in the grafted chain and the cationic dyes. Furthermore, color fastness to washing was improved for the fabric graft copolymerized with AA and methyl acrylate (MA) compared to that for the fabric grafted with only AA, because the hydrophobic parts of MA in the grafted chains caused a hydrophobic interaction with the dye in addition to ionic bonding.

(Received 13 February, 2012 ; Accepted 20 March, 2012)

1. Introduction

Poly(paraphenylene terephthalamide) fiber, referred to as para-aramid fiber, is an aromatic amide fiber with a chemical structure constructed of phenylene rings and amide bonds, as shown in Figure 1. Para-aramid fibers are one of the super fibers that have a much higher strength (>2 GPa) and elastic modulus (>50 GPa) than common fibers such as poly(ethylene terephthalate) and nylon 6 or nylon 66. Para-aramid fibers also exhibit excellent flame and heat resistance [1]. However, they are impossible to be dyed with traditional dyeing methods because of their high crystallinity and high glass transition temperatures, which limit their use in industrial applications such as building and reinforcing materials. To fully exploit para-aramid fibers in wider applications including not only industrial materials but also others such as fire protection clothing and protective uniforms, it is important to improve their dyeability.

In general, dyeing of a synthetic fiber is performed in an aqueous medium by using dyestuffs that diffuse into the free volume of the fiber. The level of diffusion increases when the temperature of the solution is higher than the glass transition temperature of the fiber. The dyestuffs are then fixed in the fiber through electrostatic

and hydrophobic interactions between the fiber and the dyestuff. However, it is difficult for dyestuffs to diffuse into a para-aramid fiber, because they have a very high glass transition temperature and crystallinity.

To improve the dyeability of para-aramid fibers, we therefore suggested modification of the fibers via electron-beam (EB)-induced graft polymerization [2-8]. EB is high-energy particle radiation. A polymeric material (fiber) irradiated with EB generates polymeric radicals through radical splitting. The fiber can then be modified by graft polymerization of a vinyl monomer with a functional group that can react with the radical on the fiber surface. The grafted polymer is then attached to the fiber surface through a covalent bond and forms a polymer layer around the fiber. This layer is more durable than those formed by other common modification processes, such as laminating or coating, in which the functional polymer layer is only physically attached to the fiber surface [9, 10].

We proposed to make a para-aramid fiber dyeable with a cationic dye by grafting onto the fiber a vinyl monomer containing an anionic group that could react with a radical on the fiber surface induced by EB irradiation. Such a fiber should be able to form an ionic bond with a cationic dye through the grafted layer around

the fiber. It has been reported that for polyester, polyamide, polypropylene, and cotton fibers, attachment of anionic groups lead to improved dyeability of the fibers with cationic dyes [11, 12]. It has also been reported that a para-aramid fiber was graft polymerized with acrylic acid (AA) by an EB irradiation technique [13].

In this study, to improve the dyeability of a para-aramid fiber, we investigated the modification of the para-aramid fiber by EB-induced graft polymerization. AA, selected as the anionic monomer containing a carboxyl group, and methyl acrylate (MA), chosen as a hydrophobic monomer, were graft copolymerized onto a para-aramid fiber to interact with a cationic dye. The effect of the chemical structure of the grafted polymer chain on the dyeability of the fiber with a cationic dye was evaluated.

2. Experimental

2.1 Materials

Kevlar[®], (800 dTex, 460 filaments, Z-twist number 150 times/m, DuPont-Toray Co.,Ltd) was used as the para-aramid fiber for all experiments. It was woven into a plain weave fabric at a woven density of 17.72 warps/cm and 9.84 wefts/cm. AA and MA were used as the monomers for the EB graft polymerization of the para-aramid fiber. The monomer structures are shown in Fig. 1. AA is a monomer bearing a carboxyl group as the anionic portion that can interact with the cationic portion of a cationic dye. MA is a hydrophobic monomer that can interact with the hydrophobic dye matrix. Methylene blue was used as the cationic dye, and its structure is shown in Fig. 1. The monomers, dyes, and other organic reagents used to wash the fabric and prepare the treatment solutions for the fabric were reagent grade materials purchased from Wako Pure Chemical Industries, Ltd. They were used without further purification.

2.2 Investigation of radicals induced by EB irradiation

Radical generation was examined for the para-aramid fibers irradiated with EB. Radical concentrations of these fibers were evaluated at 0–900 dose and 250 keV. The radicals were measured by electron spin resonance (ESR) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) methods. The ESR measurements were obtained using a JES-TE300 from JEOL Ltd. The radical concentration of the samples was calculated from the peak area of ESR absorption in the ESR spectra based on the analytical curve prepared from ESR measurements of standard benzene solutions of

Poly(paraphenylene terephthalamide) (para-aramid)

Acrylic acid (AA) Methyl acrylate (MA)

Methylene blue

Fig. 1 Chemical structures of the para-aramid fiber, monomers, and methylene blue.

2,2,6,6-tetramethylpiperidine-1-oxyl. In the DPPH method [13,14], the estimated radical amount is determined on the basis of reactivity of the radicals on the fiber surface with DPPH radicals in solution. The number of radicals on the fiber is determined from the degree of color fading of the solution containing the DPPH radicals following immersion of the fiber into the solution. In this study, the fibers were soaked in a 0.08-mM benzene solution of DPPH at 70 °C for 24 h. The degree of color fading was measured using a UV-1700 UV/VIS spectrophotometer from Shimadzu Corporation. The radical concentration was calculated from the degree of color fading by using an analytical curve prepared from measurements of the absorbance of DPPH solutions of known radical concentrations. It is possible that some of the DPPH radicals were absorbed onto the fiber without reacting with the radicals on the fiber surface. To compensate for this absorption, the degree of color fading in a DPPH solution containing a fiber that was not treated with EB irradiation was subtracted from the values determined for the solutions containing the fibers treated with EB irradiation.

2.3 Electron beam graft polymerization

The woven fabric prepared from the para-aramid fiber was soaked in a monomer solution and then squeezed with a mangle. The compositions of the different monomer solutions are listed in Table 1. The pickup ratio of the monomer solution onto the fabric was 40% for each experiment. The fabric was irradiated with EB at a dose of 450 kGy and an acceleration voltage of 250 keV by using a Curetron EBC 250-20-35 EB irradiation apparatus from NHV Corporation. The treated

Table 1 Degree of grafting, number of AA/MA units in the grafted polymer chain, and dyeing test results for para-aramid fibers graft copolymerized with AA/MA.

Molar ration in solution ^a MA:AA	Degree of grafting (%)	Grafted polymer chain (mmol g ⁻¹)		Photograph		
		MA unit	AA unit	Before dyeing	After dyeing	After washing
Untreated	-	-	-
100:1	0.95	0.127	0.001
50:1	0.72	0.078	0.008
10:1	4.34	0.393	0.099
5:1	9.94	0.862	0.350
0:1	17.6	-	2.19

^a Treatment solution of a fabric; monomer (MA and AA) 75%:methanol 16%:water 9%

fabric was washed with water at 100 °C and methanol at 60 °C for each 1 h to remove any unreacted monomer and homopolymer. The degree of grafting onto the fabric was estimated from the change in the weight of the fabric before and after the treatment.

2.4 Estimation of the chemical structure of grafted polymer chains

The chemical structures of the grafted polymer chains on the para-aramid fibers were estimated by the Boehm titration [15, 16]. The carboxyl groups of AA units in the grafted polymer chains on the para-aramid fibers were neutralized with an excess amount of NaHCO₃ by soaking the fibers in a 0.1 M NaHCO₃ aqueous solution and then stirring at room temperature for 4 h. The fiber was separated from the NaHCO₃ solution by filtration. The unreacted NaHCO₃ in the solution was neutralized with an excess amount of HCl by adding an aqueous 0.1 M HCl solution. Carbon dioxide was removed from the solution by purging with nitrogen for 3 h. Excess HCl was then titrated with a 0.005 M NaOH aqueous solution. The AA unit content in the grafted polymer chains on the fibers was calculated on the basis of results of the titration of the carboxyl groups in the grafted polymer chains. The MA unit content of the grafted polymer chains was then obtained by subtracting the AA unit amount from the weight of the grafted polymer chains on the fibers.

2.5 Evaluation of dyeability and color fastness to washing

Dyeability of the fabrics graft polymerized with AA and MA was evaluated from the degree of coloration with methylene blue. The dye solution was prepared at 1%_{owf}

(% on the weight of fabric), and its pH was controlled within 4.5–5 by adding a 3 wt% aqueous acetic acid solution and a 1 wt% aqueous sodium acetate solution. The 4 cm × 10 cm of fabric was dyed with the dye solution at a bath ratio of 1 : 60 at 60 °C for 1 h using a UR·MINI-COLOR.V_s multicoloration system from Texam Giken Co., Ltd. Color fastness to washing of the fabric was evaluated from the degree of color fading in the dyed fabric by using the washing test according to JIS L0844 A-2. The degree of coloration and color fading were quantified by the change in lightness (L*) value (an average of 5 places on the fabric) according to the L*a*b* color system, which was measured with a CM-2600d spectrophotometer from Konica Minolta Holdings, Inc.

3. Results and discussion

3.1 Generation of radicals in the para-aramid fiber using EB irradiation

The generation of radicals was evaluated for the para-aramid fibers irradiated with EB. The ESR spectrum of a fiber irradiated with EB is shown in Fig. 2. A hyperfine structure [17] was observed in the spectrum of the fiber, which indicated that the radicals generated in the fiber formed a resonance structure and moved in the molecular chain of the fiber. The amount of radicals generated in the fiber determined using the ESR and DPPH methods are plotted as a function of irradiation dose in Fig. 3. The amount of radicals determined using both methods increased with an increase in the dose. A larger amount of radical splitting is expected to occur with an increase in the absorption energy of the para-

Fig. 2 ESR spectrum for the para-aramid fiber irradiated with EB at 200 kGy.

Fig. 4 Effect of the monomer solution composition on the degree of grafting onto the para-aramid fiber.

Fig. 3 Radical concentration of the para-aramid fiber irradiated with EB.

Fig. 5 Effect of the monomer solution composition on the unit ratio in the polymer chain grafted onto the para-aramid fiber.

aramid fiber. A comparison of the radical concentrations of the fibers determined by the ESR and the DPPH methods showed that 20%–40% of the radicals generated in the fiber exhibited reactivity toward other chemicals. The unreactive radicals are most probably trapped in the crystalline region of the fiber and unable to encounter the DPPH radicals, because DPPH radicals are impossible to diffuse into the crystalline regions.

3.2 Chemical structures of the grafted polymer chains on the para-aramid fibers treated with EB irradiation

The para-aramid fiber was graft copolymerized with AA and MA to improve its dyeability. Various chemical structures of the grafted polymer chains on the fiber were constructed using monomer solutions containing AA and MA in ratios from 1 : 0 to 1 : 100. The relationship between the degree of grafting and the AA content in the fabric treatment solution is shown in Fig. 4. The degree of grafting increased with an increase in the AA content in the treatment solution. The AA and MA homopolymers were prepared by EB irradiation under the same

conditions as those employed for EB graft polymerization, and then they were tested the solubility in the solvents. Poly-AA was insoluble in the solvent, whereas poly-MA was soluble. It was considered that AA was polymerized into a cross-linked polymer or a much higher molecular weight polymer than MA by EB irradiation, while MA was polymerized into a linear polymer with low molecular weight soluble in the solvent. It was also reported that AA was polymerized into a cross-linked polymer by EB irradiation [18]. Therefore, it would be expected that when the treatment solution contains more AA, a cross-linked polymer forms more readily, which results in a higher molecular weight of the grafted polymer chain. Thus, the degree of grafting increases with an increase in the AA content in the treatment solution.

The chemical structures of the grafted polymer chains on the fibers graft polymerized with AA and MA by EB irradiation are shown in Fig. 5 as a function of the ratio of AA to MA units. In the figure, the solid line indicates the calculated trend based on the Alfery–Price

Fig. 6 L^* value of the para-aramid fiber graft copolymerized with AA/MA.

Fig. 7 ΔL^* value of the para-aramid fiber graft copolymerized with AA/MA.

Q-e values, which were obtained from the literature [19]. The dashed line shows the results obtained for polymerization initiated with the common initiator 2,2'-azodiisobutyronitrile (without grafting), which results in the formation of a linear polymer [20]. The closed circle indicates the results for polymerization (without grafting) initiated with EB irradiation under the same conditions as those employed for the graft polymerization treatment of the fabric. The open circle shows the results for the polymer grafted onto the fiber that was treated with EB irradiation. A comparison of the plots of the closed circle, the solid line, and the broken line shows that polymerization initiated with EB irradiation was the same as common radical polymerization. In contrast, the percent of the AA units in the polymer grafted onto the fiber (open circle) was greater than that in the polymer that was not grafted onto the fiber (closed circle), even though both polymers were polymerized under the same EB irradiation conditions. The former and latter were

polymerizations initiated by the radicals generated on the fiber and from the monomer, respectively, as a result of EB irradiation. Graft polymerization, therefore, may be affected by the fiber, which might for example, limit the diffusion of the monomers. Further studies are underway to clarify these issues.

3.3 Improvement in dyeability by graft copolymerizing with AA and MA

The degree of grafting, the number of AA and MA units in the grafted polymer chain, and photographs of the fabric before/after dyeing and after washing are shown in Table 1. Changes in the L^* value of the fabric before/after dyeing and after washing are also shown in Fig. 6. The fabrics that possessed grafted polymer chains containing less than 0.099 mmol/g of AA were not dyed with the cationic dye, and they had the same L^* value after dyeing as that of the untreated fabric. The fabrics that possessed grafted polymer chains containing more than 0.099 mmol/g of AA, however, were dyed to a deeper color and had a smaller L^* value compared with the untreated fabric. In Fig. 7, the change in the L^* value before and after washing (ΔL^*) is plotted for the dyed fabrics as a function of the mole fraction of AA in the grafted polymer chains of the fibers. A smaller ΔL^* value for a fabric indicates that the fabric was less decolorized after undergoing the washing test, denoting that the fabric has a higher color fastness to washing. The fabrics that possessed the grafted polymer chains containing an AA mole fraction less than 0.2 showed relatively smaller ΔL^* values compared to the other fabrics because they were not dyed and thus had little dye leaving from the fiber with washing. The fabrics that possessed the grafted polymer chains containing an AA mole fraction greater than 0.2 were dyed to a deeper color compared to the untreated fabric and thus showed relatively larger ΔL^* values. This result indicates that the dye molecules interacting with the grafted polymer chains left the fiber with washing. In these fabrics, however, the fabric that possessed the grafted polymer chains with an AA mole fraction of 0.29 showed the minimal ΔL^* value, indicating that fewer dye molecules were released from such a fiber by washing compared to the other fabrics.

3.4 Dyeing mechanism

Fig. 8 shows a schematic diagram of the dyeing mechanism for the para-aramid fiber graft copolymerized with AA and MA. In case of the untreated fiber (1), the fiber was not dyed because the dye molecules could not diffuse into the fiber and were only attached onto the fiber surface. In contrast, in the case where the fiber is graft polymerized with only AA (2), the fiber was improved in

Fig. 8 Schematic diagram of the dyeing mechanism for the para-aramid fiber graft copolymerized with AA/MA.

its dyeability with a cationic dye because the anionic groups in the grafted polymer chain interacted with the cationic parts of the dye compound. The grafted polymer chains consisting only of AA had a high concentration of anionic groups in the chain, which led to the extension of the grafted polymer chains in the water owing to repulsion between the anionic groups. The dye molecules interacted with the grafted polymer chain only through ionic bonding between the cationic portion of the dye and the anionic portion of the grafted polymer chain. Thus, the dye molecules were readily released from the fiber by washing with a detergent. In the case where the fiber was graft copolymerized with MA in addition to AA (3), the grafted polymer chains had hydrophobic MA units inserted between the anionic AA units, which led the grafted polymer chain to exist as a globule in water. The dye molecules diffused into the globule, and the hydrophobic matrix of the dye interacted with the hydrophobic portion of the grafted polymer chain in addition to ionic bonding between the cationic portions of the dye compound and the anionic portion of the grafted polymer chain. As a result, a stronger interaction was formed between the dye and the grafted polymer chain than that between the dye and the fabric graft polymerized with only AA. Therefore, in this case, color fastness to washing was improved along with dyeability with a cationic dye.

For a cotton fabric dyed with a cationic dye, it has been reported that dyeability and color fastness to washing improved when the fiber underwent chemical treatment with both hydrophobic and anionic compounds [12]. In case where the fiber was graft copolymerized

with AA and MA at a higher ratio of MA to AA (4) than that in case (3), the dye molecules diffused into the globule of the grafted polymer chain as in case (3). Most of the dye, however, formed only a hydrophobic interaction with the grafted polymer chain owing to the low concentration of anionic groups in the chain, which led to a weaker interaction between the dye and the grafted polymer chain compared to that observed in the case with a higher AA content. The dye molecules were therefore released more easily from the fiber by washing than in case (3).

4. Conclusion

To improve the dyeability of a poly(p-phenylene terephthalamide) fiber, we investigated the modification of the fiber through EB-induced graft polymerization. The generation of radicals was confirmed in the fiber irradiated with EB, and the radical concentration was increased with an increase in the dose. An estimated 20%–40% of the radicals generated in the fiber showed reactivity on the fiber surface. AA was used as an anionic monomer for graft polymerization to improve dyeability with a cationic dye. The fabric graft polymerized with AA or AA/MA was dyed to a deeper color than the untreated one. The fabrics grafted with only AA showed low color fastness to washing, while the fabric graft copolymerized with MA in addition to AA showed improved color fastness to washing. This difference can be explained by the different interactions between the dye and the anionic and hydrophobic AA and MA groups. Dyeability of the fabrics graft polymerized with the anionic monomer improved through formation of ionic bonds between the polymer chain and the cationic dye. Color fastness of the fabric grafted with AA and MA improved because the hydrophobic portions derived from the MA in the grafted polymer chains participated in hydrophobic interactions with the hydrophobic matrix of the dye in addition to ionic bonding between AA and the grafted polymer chains.

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