BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3324—3326 (1969)

Reaction of Modified Polypropylene Fiber Containing the Glycidyl Group with Several Amines and Ammonia

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(Received May 16, 1969)

Polypropylene was modified by the blending of the fine powdery copolymer of glycidyl methacrylate and divinyl benzene, and this modified polypropylene fiber was treated with diethyl amine, diethanol amine, monoethanol amine, and ammonia. The reactivity order was as follows: monoethanol amine>diethyl amine> diethanol amine=ammonia. Consequently, the resultant fiber showed water-wettability and could be dyed with an acidic dye.

Polypropylene shows poor dyeability, no water-wettability, and a waxy touch, as a result of its high crystallinity and nonpolarity. These properties are drawbacks in practical uses. In order to make polypropylene fiber dyeable with an acidic dye, the following procedures have been proposed: (1) the blending of polyvinyl pyridine,[1] (2) the blending of the styrene-glycidyl methacrylate copolymer and after-treatment with amines,[2] and (3) the grafting of glycidyl methacrylate and after-treatment with amines.[3]

One of the present authors has already reported the modification of polypropylene with a polymeric fine powder (PFPC), prepared from glycidyl methacrylate (GMA) and divinylbenzene (DVB). This powder is more thermally stable than such a linear polymer as a styrene-GMA copolymer, and it has been established that this modification is very effective in improving the dyeability of polypropylene fiber[4,5] and that the dyes having an amino group can be fixed in the substrate by the reaction between the epoxy group in the substrate and the amino group.[4,5] Therefore, it was presumed that an amine can easily react with the epoxy group. The introduction of the amino group into polypropylene is very interesting, because polypropylene may be modified to make it water-wettable, antistatic, and dyeable by an acidic dye; such dyes were inavailable in the previous studies.[4,5] Accordingly, the reactions of the polypropylene fiber modified by the blending of PFPC with some amines and ammonia were investigated by the use of the undrawn fiber as a model case. Furthermore, the dyeability of the modified fiber with an acidic dye was investigated by the use of the drawn fiber.

Experimental

Material. A commercial polypropylene pellet was blended with PFPC at 170—185°C by the use of a calender roller. The fabricating conditions and the properties of the fiber are shown in Table 1. The properties of the polypropylene were as follows:

Melt index (at 230°C, load: 2.16 kg/cm^2): 4.4 g/10 min
Specific gravity (at 23°C): 0.914

TABLE 1. THE FABRICATING CONDITIONS AND THE PROPERTIES OF THE FIBER

Sample	Fabricating conditions				PFPC content %	Fineness, denier	Epoxy value, mmol/g fiber	
	Spinning temp.°C	Drawing temp.°C	Draw ratio	Heat set			Calcd	Obsd*
PP-F-1	240	—	—	—	3	5—6	0.199	0.200
PP-F-2	270	130	4	130°C, 10 sec	3.4	5	0.224	0.221

* Determined by the modification of the HCl-Dioxane method.[3]

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[1] R. A. Bychkov and M. P. Zverev, *International Chem. Eng.*, **7**, 76 (1967).

[2] M. Kubota, M. Katayama and O. Ishizuka, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 725 (1963).

[3] Y. Iwakura, T. Kurosaki, K. Nagakubo, K. Takeda and M. Miura, This Bulletin, **38**, 1349 (1965).

[4] Y. Mizutani, *ibid.*, **39**, 1088 (1967).

[5] Y. Mizutani, *ibid.*, **40**, 1519 (1967).

PFPC was prepared by the method reported in the previous papers.[4,5] Diethanol amine (DEA), monoethanol amine (MEA), and diethyl amine (DA) were used after distillation under a reduced nitrogen atmosphere.

Procedures. The fiber (0.80 g) and an aqueous solution of an amine or ammonia were placed into a pressure bottle. A piece of glass rod was placed on the fiber in order to immerse the fiber in the solution. In order to gain analytical accuracy, the concentration of the amine or ammonia was controlled so as to be 0.4—1.6 mmol/20 m*l*. The pressure bottle was immersed in an oil bath at a definite temperature without any stirring. After a definite reaction time, the pressure bottle was rapidly cooled by water. Then the fiber was taken out and rinsed with 100 m*l* of water. A washing solution was added to the reactant solution; the quantity of amine or ammonia after the treatment was determined by pH titration with a 0.01 N aqueous solution of hydrochloric acid. The neutralization points are shown in Table 2. The preliminary experiment confirmed that Monogen-w (an emulsifier from the Daiichi Kogyo Seiyaku Co., Ltd.) did not disturb the titration. The quantity of the reacted amine or ammonia ($[A]_F$) and the reaction degree of the epoxy group in the fiber were defined as follows:

TABLE 2. THE NEUTRALIZATION POINT

Reagent	DA	DEA	MEA	Ammonia
pH	6.1	4.9	5.3	5.8

$$[A]_F = [A]_0 - [A]_t \qquad (1)$$

$$R_A = [A]_F/\text{Epoxy value of the fiber} \qquad (2)$$

$[A]_0$: Initial quantity of an amine or ammonia

$[A]_t$: The quantity of an amine or ammonia after treatment for *t* hr.

Dyeing. The fiber (50 g) was treated at 120°C for 4 hr with the following solution-mixture:

$$\text{A-solution} \begin{bmatrix} Na_2SO_4\text{: } 5\ g/l \\ \text{Monogen-w: } 1\ g/l \end{bmatrix}\text{: } 150\ ml$$

DEA : 150 m*l*

The fiber (2 g) thus treated was dyed under the conditions shown in Table 3.

Results and Discussion

PP-F-1 (undrawn fiber; see Table 1) was used to investigate the reaction. Figure 1 shows the results of the reaction. The reactivity order was as follows: MEA>DA>DEA=ammonia. Figures 2 and 3 show the effect of the molar ratio of the amine or ammonia to the epoxy group. It was established that the increase in the reactant concentration increases the $[A]_F$ and R_A values, and that when bath

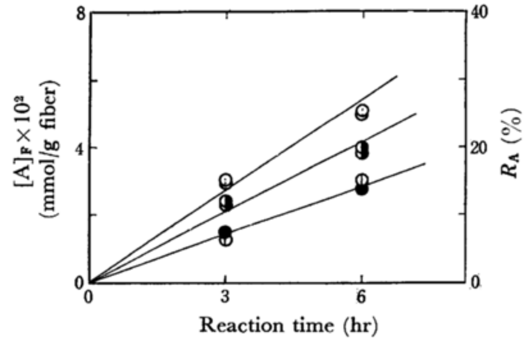

Fig. 1. The comparison of the reactivity.
○: MEA, ◑: DA, ●: DEA, ⦶: ammonia
Concentration of reagent: 0.4 mmol/20 m*l*
Reaction temperature: 120°C
Bath ratis: 25 m*l*/g fiber

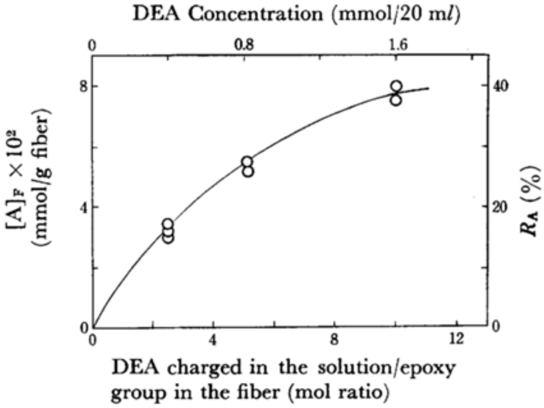

Fig. 2. The effect of DEA concentration.
Reaction temperature: 120°C
Bath ratio: 25 m*l*/g fiber
Reaction time: 6 hr

TABLE 3. THE DYEING CONDITIONS

Dye	Kayacyl Rubinol 3GS C.I. Acid Red 37 and Kayanol Floxine NK C.I. Acid Red 257	Kayanol Milling Scarlet FGW C.I. Acid Red 111	Kayakalon Scarlet GL C.I. Acid Red 317
Conditions	Bath ratio: 50 by weight Dye: 2% o.w.f. Na_2SO_4: 10% o.w.f. H_2SO_4(66° Be′): 4% o.w.f. 60°C→100°C, 15 min 100°C, 60 min	Bath ratio: 50 by weight Dye: 2% o.w.f. Na_2SO_4: 10% o.w.f. CH_3COOH: 2% o.w.f. 50°C→100°C, 15 min 100°C, 60 min	Bath ratio: 50 by weight Dye: 2% o.w.f. CH_3COOH(48%): 2% o.w.f. 50°C→100°C, 30 min 100°C, 45 min

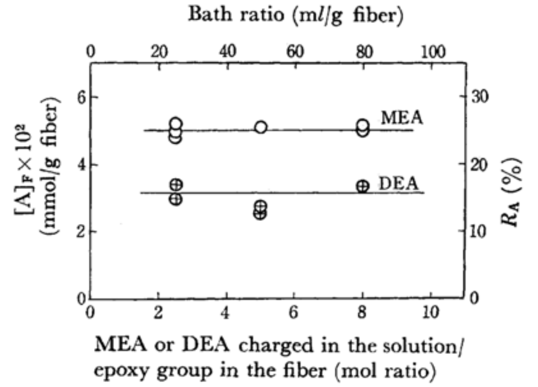

Fig. 3. The effect of the bath ratio.
Reaction temperature: 120°C
Concentration of DEA or MEA: 0.4 mmol/20 ml
Reaction time: 6 hr

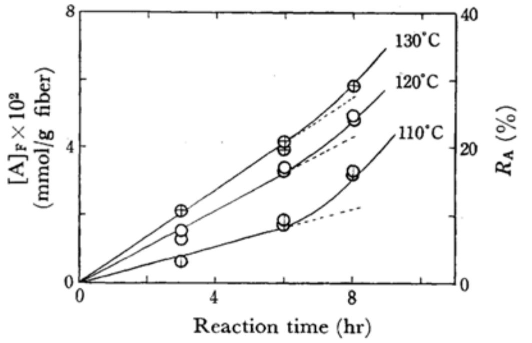

Fig. 4. The effect of the reaction temperature.
Concentration of DEA: 0.4 mmol/20 ml
Bath ratio: 20 ml/g fiber

TABLE 4. THE REACTION RATE

Reaction temperature, °C	130	120	110
$k\times10^3$, mmol/hr g fiber	7.03	5.37	2.88

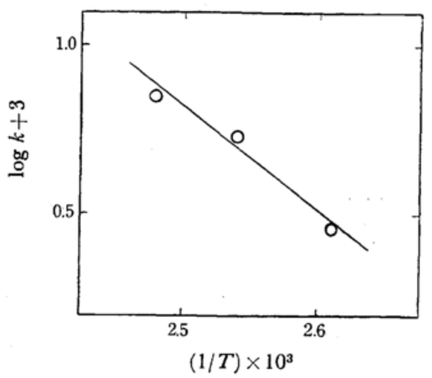

Fig. 5. The Arrhenius plot of the logarithm of the rate constant (k) against the reciprocal of absolute temperature.

TABLE 5. THE DYEABILITY AND THE DYEING FASTNESS

Dye	Kayacyl Rubinol 3GS	Kayanol Floxine NK	Kayanol Milling Scarlet FGW	Kayakalon Scarlet GL
Exhaustion %	34	49	51	59
Fastness to washing*	2—3	3	2	2—3

* Estimated by JIS L 1045—1959, MC-2 (Translated in English and published by Japanese Standards Association)

ratio increased with the constant reaction concentration, the $[A]_F$ and R_A values did not change. Figure 4 shows the effect of the reaction temperature. The reaction proceeded linearly until the reaction time had lasted 6 hr and, then, it increased. This may be attributed to the fact that the fiber became water-wettable as the reaction proceeded and to the self-catalytic effect[6] of the hydroxyl group which resulted from the reaction. It is reasonable that the reaction became more rapid with an increase in the reaction temperature. The upper limit is about 130°C because of the thermal stability of the fiber. By means of the slope of the straight line in Figure 4, the rate constant (k) was found to be as is shown in Table 4, assuming that the reaction was zero order. Figure 5 shows the Arrhenius plot; the apparent activation energy was calculated to be 14.6 kcal/mol. It was very interesting that the fiber thus treated was water-wettable and that it did not feel waxy.

PP-F-2 (drawn fiber; see Table 1) was used to investigate the dyeability with acidic dyes. Table 5 shows the dyeing results. It was confirmed that the fiber can be well dyed by the acidic dyes. However, the dyeing fastness was insufficient and must be improved much more.

Conclusion

The polypropylene fiber, modified by the blending of a fine powdery copolymer of glycidyl methacrylate and divinylbenzene, was treated with diethyl amine, diethanol amine, monoethanol amine, and ammonia. The resultant fiber could be wettable with water and dyed with acidic dye.

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[6] Y. Iwakura, T. Kurosaki, N. Ariga and T. Ito, *Makromol. Chem.*, **97**, 128 (1966).