

Properties of Acrylic Acid Grafted Polypropylene Fiber*

Waichiro TSUJI,** Tetsuo IKEDA,** Mikiko HAMANAKA**
and Yoko IKEDA**

Received March 28, 1972

As already reported,²⁾ polypropylene fibers acrylic acid grafted and aftertreated with aqueous solutions of some metallic salts showed interesting properties such as high apparent melting point or high hydrophilicity.

In this study similar research was carried out using many other kinds of metallic salts and various properties of the treated fibers including heat and light stabilities were examined. Heat stability was somewhat improved using some metallic salts, but light stability was very much decreased in all cases. But both heat and light stabilities were very much increased by acrylic acid grafting and aftertreating with tris(1-aziridinyl) phosphine oxide (APO).

INTRODUCTION

Synthetic fibers generally have many desirable properties, but lack of hydrophilic property is a shortcoming for some uses. Some synthetic fibers have relatively low melting point or softening temperature and their practical uses are subjected to some limitation. Therefore, it is an important problem to improve the hydrophilicity and elevate the melting point of some synthetic fibers.

In relation to these problems, E. E. Magat *et al.*¹⁾ reported very interesting result that, by acrylic or maleic acid grafting and aftertreatment with aqueous solutions of some metallic salts, increased moisture regain, high wet crease recovery, low electrical resistance and high apparent melting point could be given to nylon 66, though more detailed practical properties of those fibers have not yet reported.

Prior to this, we had carried out the researches on the chemical modification of hydrophilic fibers such as cotton and polyvinyl alcohol fiber by graft copolymerization, and further taken up the grafting onto some hydrophobic fibers from the viewpoint above mentioned. Thereupon, the interesting method developed by E. E. Magat *et al.*¹⁾ was applied to polypropylene and polyvinyl chloride fibers in order to examine in more detail the effect of the treatment on the fiber properties.

Some results were already reported²⁾ on the tensile, thermal and hygroscopic properties of polypropylene and polyvinyl chloride fibers grafted with acrylic acid and aftertreated with aqueous solution of metallic salts, *etc.*

* This paper was read in the 10th International Chemical Fiber Conference in Dornbirn, Austria, 21-23th, September, 1971, the major part of which was published in German in *Lenzinger Berichte*, **32**, 106 (Dec. 1971).

** 辻和一郎, 池田徹雄, 濱中箕喜子, 池田洋子: Laboratory of Fiber Chemistry, Institute for Chemical Research, Kyoto University, Uji, 611, Kyoto

Graft copolymerization of acrylic acid was carried out using Co-60 γ -ray irradiation method and grafted fibers were aftertreated with aqueous solutions of Na_2CO_3 , $\text{Ca}(\text{CH}_3\text{COO})_2$, NH_4Cl or tris (1-aziridiny) phosphine oxide (APO). Dry and wet tensile strengths and knot strength were almost unchanged by the grafting and aftertreatment, but heat shrinkage of fibers was remarkably decreased and apparent melting point was highly elevated by these treatments. Thus, for example, 25% grafted and aftertreated polypropylene fibers did not shrink more than 10% and did not break at 200°C or over (Fig. 6). By the acrylic acid grafting and Na salt aftertreatment, moisture regain and dyeability of polypropylene fiber were remarkably increased and generation of frictional electricity was very much suppressed, while it was noted that tensile strength, modulus and dimensional stability in wet state were not reduced.

Thereafter, we have continued similar researches using polypropylene fiber, acrylic acid and many other kinds of aftertreating agents in order to obtain more detailed informations on the properties of the treated fibers including heat and light stability. The stability of polypropylene fiber to heat and light is insufficient. In this respect, Gagliardi³⁾ found that, by the treatment of polypropylene fiber with suitable phosphoric, sulfonic or carboxylic acid compound and some metallic salts, the lowering of its tensile strength by heating or Fade-Ometer exposure was reduced. While, it was reported in USSR⁴⁾ that, by the grafting of acrylonitrile, methyl-vinyl-pyridine or acrylic acid, the light stability of polypropylene fiber was remarkably improved, though its heat stability (100°C air) was rather decreased by the grafting. But in that work the effect of the treatment with metallic salts after grafting was not examined.

EXPERIMENTAL

1. Graft copolymerization of acrylic acid (AA) onto polypropylene (PP) fabric and monofilament

After pre-irradiation with Co-60 γ -ray in vacuum (dose rate 7.71×10^4 r/hr, total dose 1.54×10^5 r), AA aqueous solution in the case of fabric and water-dioxane (30/70 wt. %) solution in the case of monofilament were added and heat polymerized under vacuum of 10^{-4} mmHg. Homopolymer was removed by washing with tap water. Ratio of the weight increase to the weight of original sample was assumed as % grafting.

2. Aftertreatment of grafted PP fiber

AA grafted PP fabrics were treated with 1% aqueous solution of Na_2CO_3 at 60°C for 1 hr. After the treatment with Na_2CO_3 solution they were treated with 1% aqueous solutions of many kinds of metal acetates at 60°C for 1 hr. In the case of Al and Sn of which metal acetates were insoluble or poorly soluble in water, $\text{Al}(\text{CH}_3\text{COO})_3$ and $\text{Sn}(\text{SO}_4)_3$ and SnCl_4 were used respectively. In the case of monofilament 5% solutions were used at 80°C for 1 hr. By these aftertreatment carboxyl groups on the grafted chains were converted into metallic salt form.

In the case of the aftertreatment with tris(1-aziridiny)phosphine oxide (APO), AA grafted PP fibers were impregnated with dimethyl formamide solution of APO and $\text{Zn}(\text{BF}_4)_2$ catalyser at room temperature for about 15–20 hrs (pick up was about 100% for fabric and was not determined for monofilament), cured at 120°C for 10 min. after

drying at 90°C for 10min., then thoroughly water rinsed. The weight increase after drying was determined as APO add-on.

3. Apparent melting point

Sample was heated at the rate of about 5°C/min under a slight load (0.7 g) and the fiber breaking temperature was determined as apparent melting point.

4. Density

Fiber density was measured by density gradient tube method at 30°C using monochlorobenzene-toluene or carbon tetrachloride-toluene medium.

5. Moisture regain

After drying at 40°C under vacuum, the sample was kept at 20°C. 65% RH for 100 hrs and weight increase was determined.

6. Water absorption

Sample was immersed into water at 30°C for 24 hrs and weight increase was determined after wiping off the excess water on surface with filter paper.

7. Heat stability

Sample fabric was heated at 100°C in air circulating type dryer for various hours and the tensile strength of warp yarn was determined.

8. Light stability

Sample fabric was exposed to sunlight or xenon lamp light for different lengths of time and the tensile strength of warp yarn was determined after each exposure.

RESULTS AND DISCUSSION

1. Properties of PP fibers treated with metallic salts after AA grafting

Some examples of graftcopolymerization of AA onto PP fabric using Co-60 γ -ray preirradiation method were shown in Table 1.

a) *Moisture regain and water absorption*

Moisture regains of AA grafted PP fabrics aftertreated with various kinds of metallic salts are shown in Table 2 and Fig. 1. It is noted that the samples treated with Na_2CO_3 show remarkably high moisture regain.

Similar results are shown in the case of water absorption (Fig. 2). PP fabrics treated with Na_2CO_3 after 10–15% AA grafting show the same values of moisture regain and water absorption as cotton.

Relating to the improved hydrophilicity, the frictional static electricity of AA grafted and Na-salt treated PP filament is very much reduced as shown in Fig. 3.

b) *Density*

Though fiber density is increased by AA grafting and metallic salt treatment, these modified fibers have still lower density than many other kinds of textile fiber as shown in Fig. 4.

Table 1. Some Examples of Graftcopolymn. of AA onto PP Fabric Using ^{60}Co Gamma-ray Pre-irradiation Method.

Pre-irradiation in vacuum at room temp.

Dose rate : 7.71×10^4 r/h.Total dose: 1.54×10^5 r.Polymn. temp. : 60°C .

Conc. of AA aq. soln. (%)	Polymn. time(hr.)	% Grafting
10	0.5	7.7
10	0.5	8.3
10	1.5	9.4
10	1.5	10.4
10	2.5	16.4
10	2.5	17.4
15	1.5	23.9
15	1.5	22.7
15	2.5	27.1
15	2.5	28.3
20	1.5	39.2
20	1.5	39.0

Table 2. Moisture Regain (%) of AA Grafted and Metallic Salts Treated PP Fabrics.

Type	Metallic salt	% Grafting		
		9.6~10.4	15.2~16.6	21.6~22.1
PA ^{a)}	Control	1.2	2.8	3.3
PA(Na)	Na_2CO_3	3.1	14.3	18.9
PA(Mg)	$\text{Mg}(\text{OAc})_2$	—	6.4	5.6
PA(Al)	$\text{Al}(\text{OAc})_3 + \text{Al}_2(\text{SO}_4)_3$	1.2	4.4	5.2
PA(Ca)	$\text{Ca}(\text{OAc})_2$	1.7	5.5	6.6
PA(Ni)	$\text{Ni}(\text{OAc})_2$	1.9	4.9	7.3
PA(Cu)	$\text{Cu}(\text{OAc})_2$	3.3	3.2	5.2
PA(Zn)	$\text{Zn}(\text{OAc})_2$	1.4	3.9	5.0
PA(Zr)	$\text{Zr}(\text{OAc})_2$	2.9	2.6	—
PA(Cd)	$\text{Cd}(\text{OAc})_2$	1.3	4.9	5.2
PA(Sn)	SnCl_4	1.1	4.1	6.5
PA(Ba)	$\text{Ba}(\text{OAc})_2$	1.0	4.6	5.0
PA(Pb)	$\text{Pb}(\text{OAc})_2$	0.9	2.9	6.6

a) AA grafted PP fabric.

c) Apparent melting point

As shown in Figs. 5, 6, and 7, apparent melting point (breaking temperature) is remarkably elevated by AA grafting and especially by metallic salt aftertreatment.

d) Heat stability

PP molecule has number of tertiary carbon atoms in the main chain which are apt to be attacked by oxygen, so the stability of PP against oxidation is rather insufficient.

Properties of Acrylic Acid Grafted Polypropylene Fiber

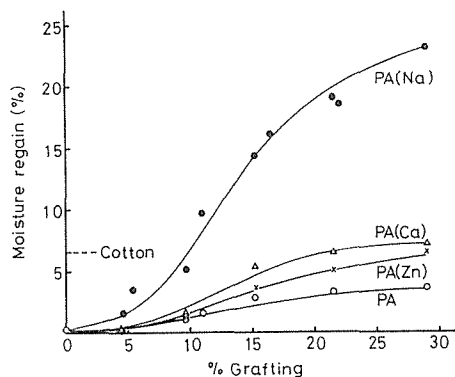


Fig. 1. Moisture regain of AA grafted and metallic salt treated PP fabric.

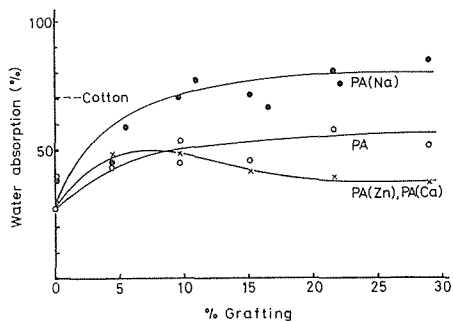


Fig. 2. Water absorption of AA grafted and metallic salt treated PP fabric.

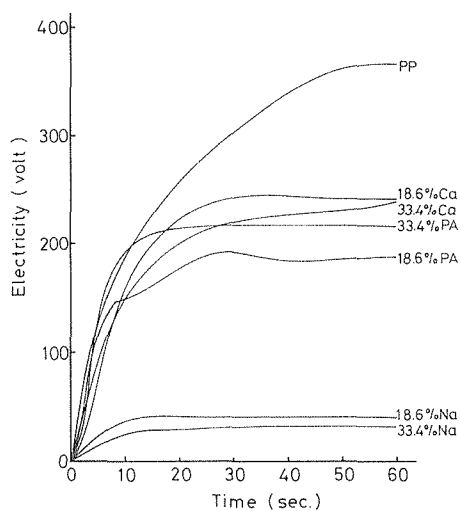


Fig. 3. Frictional static electricity of AA grafted and metallic salt treated PP monofilament.

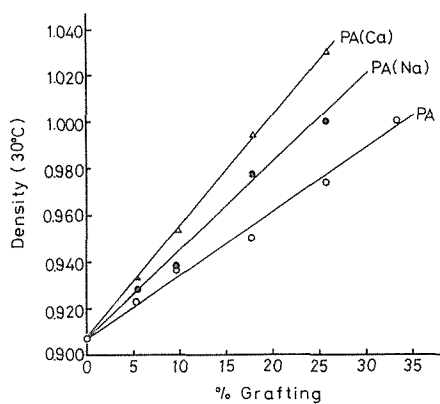


Fig. 4. Density of AA grafted and metallic salt treated PP monofilament.

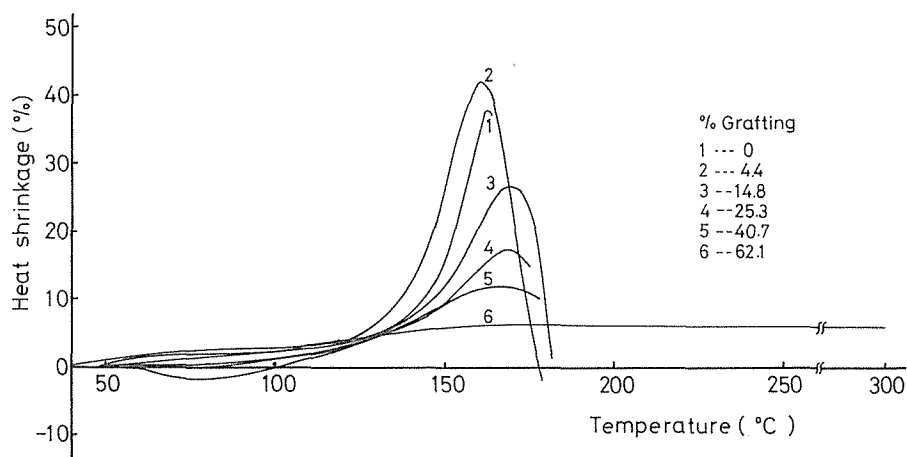


Fig. 5. Heat shrinkage of AA grafted PP fiber.

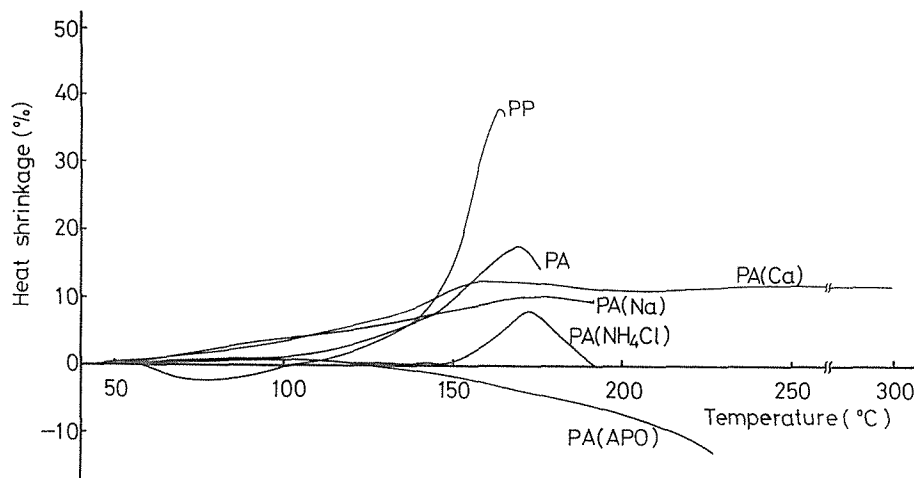


Fig. 6. Heat shrinkage of 25.3% AA grafted and aftertreated PP fiber.

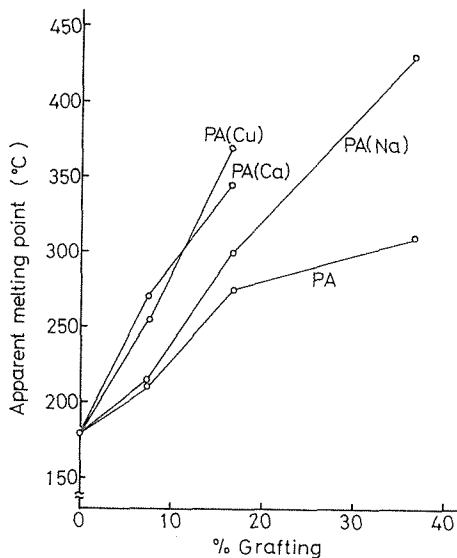


Fig. 7. Apparent melting point of AA grafted and metallic salt treated PP monofilament.

It is known that this oxidation is accelerated by heat or light. It is undesirable for practical use that fiber is apt to be deteriorated by heat or light exposure. Therefore, it is interesting and important to examine the effect of the chemical modification on heat or light stability of PP fiber.

The effect of AA grafting on the heat stability of PP fiber is shown in Fig. 8. With the increase of the degree of grafting, the tensile strength loss by heat exposure is rather increased as previously reported.⁴⁾

Then the effect of the aftertreatment with various metallic salts was examined using PP fabrics AA grafted about 10, 15 and 22%. As typical example, the results in the

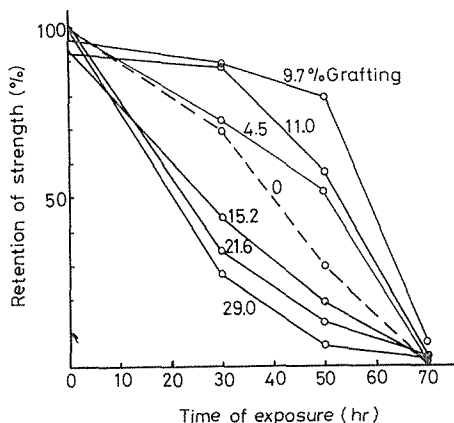


Fig. 8. Retention of warp tensile strength of AA grafted PP fabric after heat exposure at 100°C.

case of about 16% grafting are shown in Fig. 9. Ca, Zn, Ba and Ni salts give some protective effects. Cu, Co, Mn and Cr salts gave severe reverse effect and were not shown in Fig. 9.

In the case of about 10% grafting the effects of metallic salts aftertreatment were not evident, and in the case of about 22% grafting the effects were almost similar to the case of 16% grafting, as shown in Fig. 10 for Ca salts.

e) *Light stability*

The tensile strength of warp yarn of PP fabrics AA grafted and treated with metallic salts was measured after exposure to sunlight for 135 hrs. The results for about 13% grafted sample was shown in Table 3, as relative value to the tensile strength of the original (ungrafted) PP sample.

It is noted that the AA grafted or metallic salt aftertreated samples shows very lower

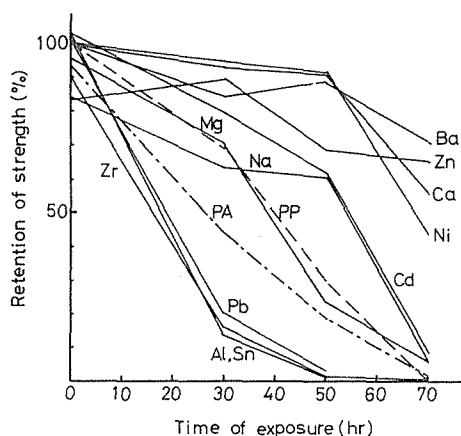


Fig. 9. Retention of warp tensile strength of AA grafted and metallic salt treated PP fabric after heat exposure at 100°C (15.2 ~16.6% grafting).

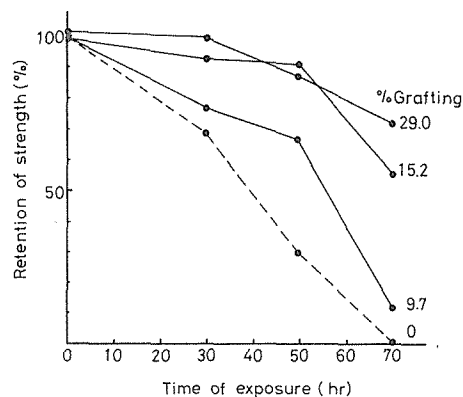


Fig. 10. Retention of warp tensile strength of AA grafted and Ca(OAc)₂ treated PP fabric after heat exposure at 100°C.

Table 3. Effect of Sunlight Exposure on the Warp Tensile Strength of the AA Grafted and Metallic Salts Treated PP Fabrics.

(12.6~13.5% grafting)

Metallic salt	Sunlight exposure	
	0 hr	135 hr
Original PP	100	29.4
Control	73	1.5
Na	89	3.7
Mg	90	1.4
Al	75	2.2
Ca	89	1.3
Ni	88	8.3
Zn	90	1.7
Zr	74	1.3
Cd	82	1.4
Sn	63	1.2
Ba	85	2.1
Pb	87	3.3

light stability rather than untreated PP. On the samples which had about 8 and 20% grafting, similar tests were carried out, but the results obtained were almost the same as the case of 13% grafting.

Tests were also carried out using xenon lamp and almost similar tendency was found as in the case of sunlight exposure.

2. Properties of PP fiber treated with tris(1-aziridinyl)phosphine oxide (APO) after AA grafting

As above described, Gagliardi³⁾ found that PP fibers treated with butyl acid phosphate and metal acetate salts showed improved stability to heat or light in the cases of Ni, Cd, Cr or Zn acetate. It is well known that APO, which contains phosphorus in the molecule, shows flame proof and anti-crease effect on cellulose fiber. In our previous work, it was found that by the APO treatment after AA grafting the crease recovery of cotton fabric⁵⁾ and the thermal properties of PP Fiber (Fig. 6)²⁾ were remarkably improved.

Further, we carried out the research on the effect of APO treatment after AA grafting on the heat or light stability and other properties of PP fiber.

Figure 11 shows the relation between the concentration of APO solution and weight increase of treated PP fabric having different % grafting. The weight increase of original (ungrafted) PP fabric by APO treatment is low. On the other hand the weight increase is fairly high for grafted fabrics. Though it is difficult to presume precisely the chemical structure resulted by the reaction of grafted AA chain with APO, it is roughly estimated from the values of % grafting and weight increase by APO aftertreatment, that 2 ethyleneimine rings out of 3 of APO molecule may be reacted with carboxyl groups of the grafted chains in the form of intramolecular crosslinkage.

a) Moisture regain

Moisture regain of PP fabrics treated with APO after AA grafting is shown in Fig.

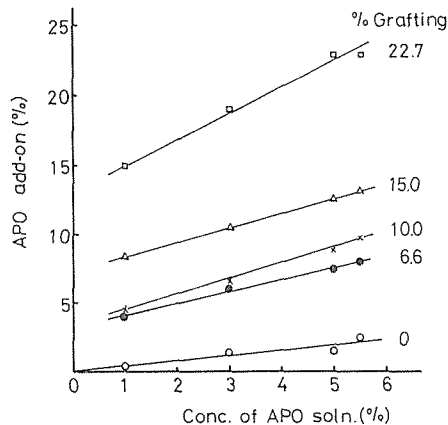


Fig. 11. Weight increase of AA grafted PP fabric by APO treatment.

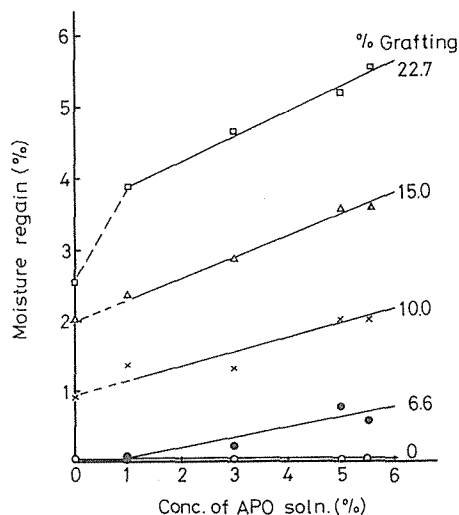


Fig. 12. Moisture regain of AA grafted and APO treated PP fabric.

12. By the APO aftertreatment the moisture regain of AA grafted PP is fairly increased.

b) *Density*

Density values of PP monofilaments AA grafted and aftertreated with 5% APO solution are shown in Fig. 13 together with the values for AA grafted samples.

c) *Apparent melting point*

Apparent melting point is remarkably improved by AA grafting and aftertreatment with APO (Fig. 14).

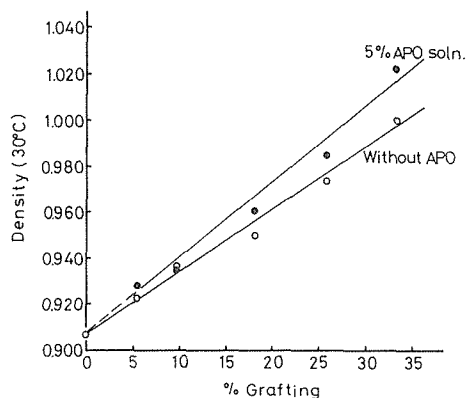


Fig. 13. Density of AA grafted and APO treated PP monofilament.

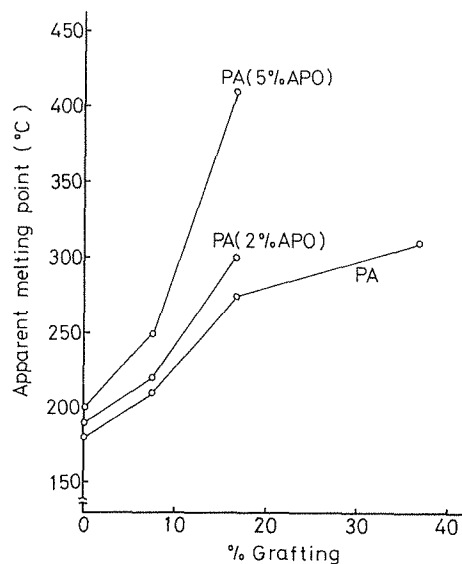


Fig. 14. Apparent melting point of AA grafted and APO treated PP monofilament.

d) *Heat stability*

As shown in Fig. 15, the heat stability of ungrafted PP fiber is somewhat increased by APO aftertreatment, but their tensile strengths are almost lost after heating at 100°C for 70 hrs., perhaps chiefly because of the little quantity of APO add-on.

On the other hand, if the AA grafted PP fiber is treated with APO, very remarkable improvement of heat stability was obtained as shown in Fig. 16, especially in the case of 15% grafting. In this case the effect of APO concentration is small. Even though the % grafting is more increased (*e. g.* 22.7%), the result is almost the same as in the case of 15% grafting.

e) *Light stability*

As in the case of heat stability, the stability of ungrafted PP fiber to sunlight is hardly improved by APO treatment, but AA grafted PP fiber shows highly improved sunlight stability by APO treatment, especially in the case of % grafting higher than 10% (Table 4). Using xenon lamp, almost the same result was found.

From the standpoint of heat and light stability, about 15% AA grafted fabric seems to be most suitable, of which the hand, color and tensile properties are almost as same as original PP fabric.

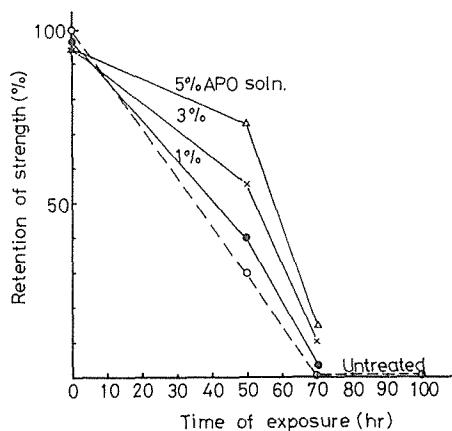


Fig. 15. Retention of warp tensile strength of APO treated PP fabric after heat exposure at 100°C.

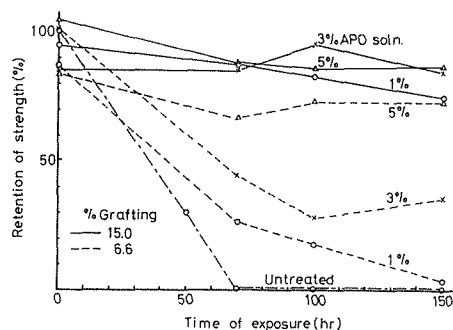


Fig. 16. Retention of warp tensile strength of AA grafted and APO treated PP fabric after heat exposure at 100°C.

Properties of Acrylic Acid Grafted Polypropylene Fiber

Table 4. Retention of Warp Tensile Strength of PP Fabric AA Grafted and Aftertreated with APO after Exposure to Sunlight for Different Lengths of Time.

%Grafting	Conc. of APO soln(%)	Sunlight exposure		
		0 hr	135 hr	280 hr
0	—	100	29	2.7
0	1	97	30	6.3
	3	94	44	12.9
	5	94	46	14.8
	5.5	99	44	18.5
6.6	1	87	46	26.5
	3	101	62	33.8
	5	83	79	59.5
	5.5	82	84	56.1
10.0	1	106	61	39.4
	3	94	73	61.6
	5	98	83	79.2
	5.5	97	89	78.0
15.0	1	94	65	53.5
	3	85	82	81.8
	5	104	90	87.5
	5.5	108	96	89.1
22.7	1	106	66	62.1
	3	87	69	61.0
	5	88	78	67.6
	5.5	91	84	81.8

REFERENCES

- (1) E. E. Magat, I. K. Miller, D. Tanner and J. Zimmerman, *J. Polymer Sci.*, **C. No. 4**, 615 (1963); D. Tanner (to du Pont), U. S. Pat., 2, 999, 056 (Sep. 5, 1961).
- (2) W. Tsuji, T. Ikeda and Y. Kurokawa, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 87 (1967); *J. Soc. Fiber Sci. Tech., Japan*, **23**, 327, 335 (1967).
- (3) D. D. Gagliardi, *Amer. Dyest. Repr.*, **54**, p. 472 (1965); USP 3, 298, 861 (1967), *C. A.* **66**, 66676u (1967).
- (4) Jung-Jui Wu, A. A. Konkin and Z. A. Rogovin, *Khim Volokna*, **No. 6**, 14 (1964); R. M. Moncrieff, *The International Dyer and Textile Printer*, 546 (Apr. 2, 1965).
- (5) W. Tsuji, *Annual Report Inst. Chemical Fiber, Kyoto Univ.*, **27**, 39 (1970).