

Improvement of Hydrophilicity of Polypropylene by Liquid-Phase Mutual Irradiation of Acrylics

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Synopsis

N-butanol was found to promote the inclusion of methyl acrylate and methyl methacrylate in polypropylene, but did not affect the uptake of acrylic acid in the polymer. Polymerization of the monomers was, however, not significantly affected by the use of this swelling agent. The monomer exchange process followed by a liquid phase mutual irradiation has proved to be very effective in enhancing the polymerization of all three monomers on polypropylene. Optimum radiation doses for effective polymerization of the monomers were found to be around 3.2 Mrad for methyl acrylate and around 4.8 Mrad for methyl methacrylate and acrylic acid. Surface wettability of the film and moisture regain of the fiber were tremendously improved with all monomers regardless of the swelling agent and temperatures. Also, a low radiation dose of 1.6 Mrad was as effective as the higher doses. Methyl acrylate and methyl methacrylate modified fibers showed no marked changes in strength and elongation, but did result in a harsher hand. Acrylic acid modified fibers increased greatly in elongation, decreased to a greater extent in strength, and softened in hand.

INTRODUCTION

Polypropylene has excellent chemical resistance and good thermal insulation characteristics and is the lightest of all commercial textile fibers. The mechanical strength of polypropylene is comparable to both dacron and nylon 6, and is therefore much stronger than orlon. Its elongation and elastic recovery is also as superior as those of nylon. In spite of its low cost and growing use in home furnishing and industrial applications, it has had very limited use as an apparel fiber in the United States. This is probably because of its hydrophobic nature, which results in difficulty in dyeing, poor water adsorption, a buildup of static electricity, and a greasy hand. In addition, polypropylene also has low softening and melting points and the inability to durably hold chemical finishes.

Radiation-induced polymerization in polypropylene can be found in many patents because of the possibility of adding new properties from the added monomer without drastically changing the properties of the polypropylene backbone. However, research efforts in applying radiation-induced polymerization of monomers in polypropylene have been limited in comparison to the tremendous amount of research dedicated to modifying other synthetic fibers.

Armstrong and Walsh¹ copolymerized polypropylene fibers with methyl acrylate, ethyl acrylate, vinyl acetate, and acrylonitrile in the vapor phase

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by mutual γ -irradiation. They found that the modified fibers dyed well with disperse dyes, that their melting points were significantly greater than that of unmodified polypropylene, and that their moisture regains increased slightly. This was accompanied by no marked changes in strength or elongation.

Since then, others have studied the optimum conditions for polymerization in polypropylene films. Munari et al. studied the polymerization yield and rate of polymerization of various concentrations of 4-vinyl pyridine in ethanol and in benzene in preirradiated polypropylene films.² With both solutions, polymerization yield increased with monomer concentration. However, in benzene (a swelling agent for polypropylene), the time necessary to reach the limiting values of polymerization decreased as the amount of solvent increased. Burchill et al. polymerized methyl methacrylate in polypropylene film in methanol solutions open to air using a mutual γ -irradiation method.³ They found that no polymerization occurred for solutions containing less than 10% water, presumably because water lowers the amount of oxygen in the monomer solution.

Sundari polymerized 1-vinyl-2-pyrrolidone, acrylic acid, and acrylamide in preirradiated polypropylene fibers both in the presence and absence of air.⁴ Polymerization increased directly proportional to the logarithm of both dose and reaction time. It also increased with reaction temperature in the case of irradiation in the presence of air. Melting point and moisture regain increased directly with polymerization of all monomers, with 1-vinyl-2-pyrrolidone- and acrylic-acid-modified fibers showing the greatest increases. Dye adsorption also increased in all cases.

Radiation-induced polymerization in polypropylene has also been applied to novel uses. Liddy et al. have polymerized *p*-nitrosytrene in polypropylene in order to covalently bind enzymes to produce active, water-insoluble conjugates.⁵ Rangajec et al., have polymerized a UV stabilizer in polypropylene film using mutual γ -irradiation.⁶

Since research in polypropylene has been scattered in terms of the effects of monomers, irradiation methods, and the form of the polypropylene as possible ways of modifying and improving its properties, more in-depth studies are needed to extend the potential applications of this polymer. The present study intends to explore the effectiveness of a swelling agent and a modified mutual irradiation process in polymerizing acrylics in polypropylene to improve its hydrophilicity.

EXPERIMENTAL

Polypropylene film having a thickness of 3.5 mil was obtained from Hercules. Samples of size 1 cm \times 5 cm (0.04 g) were rinsed with 1,1,2-trichloro-1,2,2-trifluoroethane. Polypropylene filaments (0.04 g) were obtained as untwisted warp yarns from a plain weave fabric. Both films and fibers were dried under vacuum at 105°C for 3 h before use. The solvents and monomers used were reagent grade and were used without further purification. Inhibitors were removed from the monomers by filtration over aluminum oxide.

The modified mutual irradiation method involved preliminary swelling of the fibers, subsequent exchange with monomer, followed by mutual ir-

radiation in an aqueous monomer solution. *n*-Butanol was used as the swelling agent since alcohols up to heptanol were found to be most efficient at polymerizing styrene in polypropylene powder.⁵

Samples were immersed in *n*-butanol for either 24 h at 25°C, 0.5 h at 60°C, or 0.5 h at 100°C. Solvent uptake (*S*) was calculated as

$$S = \frac{W_s - W_0}{W_0} \times 100$$

where W_0 is the initial dry weight of the sample and W_s is the weight of the sample after immersion in *n*-butanol. Samples were blotted dry between filter papers before weighing. They were then exchanged with concentrated monomer solution at a substrate:monomer ratio of 0.002 (w/v) for 6 days. Monomer uptake (*M*) was calculated as

$$M = \frac{W_m - W_0}{W_0} \times 100$$

where W_m is the blotted dry weight of the sample after monomer exchange and W_0 is again the initial dry weight of the sample.

Samples were placed in a glass tube, filled with a 1M aqueous monomer solution containing 0.4% (w/v) copper sulfate as inhibitor, and irradiated. A cobalt-60 gamma radiation source was used. Four doses of approximately 1.6, 3.2, 4.8, and 6.3 Mrad were obtained by varying the length of irradiation at 9 rad/s. After irradiation, samples with acrylic acid (AA) were extracted with methanol for 24 h, and those with methyl acrylate (MA), or with methyl methacrylate (MMA), were extracted with acetone for up to 72 h. These extractions were necessary in removing residual monomers, oligamers, and homopolymer. The extent of polymerization (*P*) was calculated as

$$P = \frac{W_p - W_0}{W_0} \times 100$$

where W_p is the extracted dry weight of the sample.

Surface wettability was measured by water contact angles. Five water contact angle measurements were taken on each film using 0.5 μ L triply-deionized-distilled water. Moisture regain (MR) values were calculated for all fibers as follows:

$$MR = \frac{W_c - W}{W} \times 100$$

where W_c is the sample weight after conditioning 4 days at 20°C and 65% relative humidity. W_p is the extracted dry weight of the sample. Single fiber tensile properties, i.e., the load at yield, extension at yield, breaking load, and extension at break, were determined with 10 irradiated fibers from each sample using an Instron.

TABLE I
 Solvent and Monomer Uptake of Fibers

Solvent temp (°C)	Solvent uptake (%)	MA uptake (%)	MMA uptake (%)	AA uptake (%)
No swelling	—	2.6	0.4	25.6
25	4.1	8.3	4.8	32.2
60	3.8	3.8	4.4	27.0
100	7.2	6.6	7.1	18.0

RESULTS AND DISCUSSION

The use of *n*-butanol as a swelling agent was examined by the extent of the solvent and the monomers incorporated in the substrates. Table I shows the weight increases of polypropylene (PP) fibers after the immersion in *n*-butanol and those after the exchange in the monomers. *n*-Butanol treatment significantly increased the uptakes of MA and MMA but did not seem to affect the incorporation of AA in the PP substrates. A much higher uptake of AA than the other two monomers was observed at each temperature. Solvent uptake at 100°C was higher than that at either 25°C or 60°C. Although higher temperature correlated with small increases in solvent uptake, monomer uptakes for all three monomers were not affected by temperature. The incorporation of acrylic acid actually decreased with the increasing temperature.

The extent of polymerization is shown in Table II. In general, the extent of polymerization was much higher for AA than for either MA or MMA. With all three monomer systems, no specific trend was found among the three swelling temperatures. This confirms the earlier observation that monomer uptake is not affected by temperature. It appears that the optimum dose for the highest polymerization yield of all monomers is around

 TABLE II
 Extent of Polymerization (*G*) of PP Fibers

Solvent temp (°C)	Dose (Mrad)	Monomers		
		MA	MMA	AA
No swelling	1.6	5.3	6.4	36.4
	3.2	19.0	9.0	66.7
	4.8	10.1	1.2	70.2
	6.3	10.5	7.4	68.1
25	1.6	11.0	9.3	44.4
	3.2	26.5	9.8	64.1
	4.8	19.2	10.2	75.8
	6.3	13.9	6.2	71.1
60	1.6	7.0	7.1	42.1
	3.2	9.0	6.1	59.5
	4.8	28.0	10.4	70.2
	6.3	14.9	9.7	72.3
100	1.6	6.9	1.7	36.0
	3.2	18.0	—	58.3
	4.8	14.7	10.0	68.1
	6.3	17.6	16.3	66.6

TABLE III
 Mutual/Post-Irradiation Ratio

Swelling temp (°C)	Dose (Mrad)	Monomers		
		MA	MMA	AA
No swelling	1.6	1.0	15.0	0.4
	3.2	6.3	21.5	1.6
	4.8	2.9	2.0	1.7
	6.3	3.0	17.5	1.7
25	1.6	1.3	0.9	0.4
	3.2	2.2	1.0	1.0
	4.8	1.3	1.1	1.4
	6.3	0.7	0.3	1.2
60	1.6	0.8	0.6	0.6
	3.2	1.4	0.4	1.2
	4.8	6.4	1.4	1.6
	6.3	2.9	1.2	1.7
100	1.6	0.1	-0.7	1.0
	3.2	1.7	—	1.2
	4.8	1.2	0.4	2.8
	6.3	1.7	1.3	2.7

5 Mrad. This result from the modified mutual irradiation method is in contrast to the linear relationship found between polymerization and logarithm of dose by the preirradiated method.⁴

The extents of polymerization for all three monomers being much higher than their monomer uptakes indicates that both the premonomer exchange and the mutual irradiation procedure were effective. Since the premonomer exchange process is usually associated with a post-irradiation process, an assessment of the relative effects of the mutual and post-irradiation methods could give further insight into this new combined approach. Under the assumption that all incorporated monomer polymerizes during irradiation, and remains in the polymer substrate, the effectiveness of this mutual irradiation process vs. a post-irradiation process on inducing polymerization can be described as $(G - M)/M$ (Table III). In most cases, a dose of 3.2 Mrad or higher resulted in equal or higher polymerization from the mutual irradiation than from the post-irradiation process. It seems to suggest that the effects of mutual and post-irradiation processes are similar for each of the three monomer systems.

The moisture regain of the untreated PP fibers is 0.2%. All three monomers greatly increased the moisture regain of PP fibers, with AA showing the greatest increases (Table IV). For AA and MA, moisture regain was found to be highest for the 25°C swelling temperature. For MMA, the 25°C and 60°C swelling temperatures affected moisture regain similarly, with the 60°C samples being slightly higher. This correlates with the extent of polymerization data in that polymerization was generally lower for those samples swollen at 100°C.

The water contact angle of the untreated PP film is 101°. Those of the modified samples are shown in Figure 1. All were considerably less than 101°, with MA films producing the lowest values at a dose of 4.8 Mrad. Films modified with AA and MA had better wettability as the dose in-

TABLE IV
Moisture Regain of Modified Fibers (Control < 0.2%)

Solvent temp (°C)	Dose (Mrad)	Monomer		
		MA	MMA	AA
No swelling	1.6	2.1	1.8	3.3
	3.2	2.7	2.1	4.7
	4.8	1.6	2.7	5.4
	6.3	2.2	2.1	4.9
25	1.6	2.9	2.9	4.6
	3.2	2.3	2.4	4.8
	4.8	3.6	3.0	5.2
	6.3	1.0	2.7	4.8
60	1.6	2.2	4.7	4.2
	3.2	2.2	2.4	4.7
	4.8	2.4	3.1	4.7
	6.3	1.7	2.9	4.5
100	1.6	2.1	1.9	3.3
	3.2	1.9	1.1	4.5
	4.8	1.8	2.2	5.1
	6.3	1.3	1.7	4.3

creased. Surface wettability for samples modified with the same monomer were similar, regardless of temperature.

Due to the high molecular weight of polymers, polymers often exhibit drastic changes in their physical properties for only minor chemical modifications. Thus, the tensile properties for these modified fibers were examined (Figs. 2-5). The untreated PP fibers had a 1.5% extension at yield, a 3.7 g load at yield, a 21.2% extension at break, and a 39.5 g load at break. The MA- and MMA-modified fibers decreased slightly in extension at yield, extension at break, and load at break. This is an expected consequence of exposure to γ -radiation, and acceptable for most applications in such small decrements. The AA-polymerized fibers showed the only significant

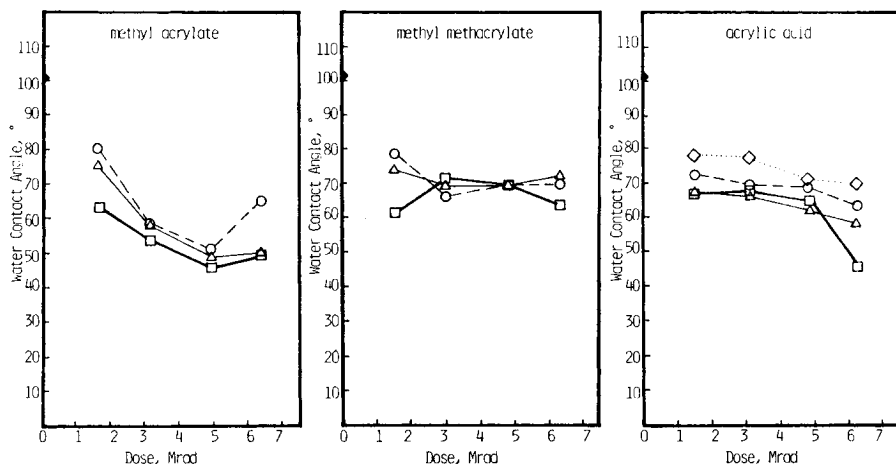


Fig. 1. Water contact angles of modified films: (○- - -) 25°C; (△—) 60°C; (□—) 100°C; (◇···) no solvent; (◆) control.

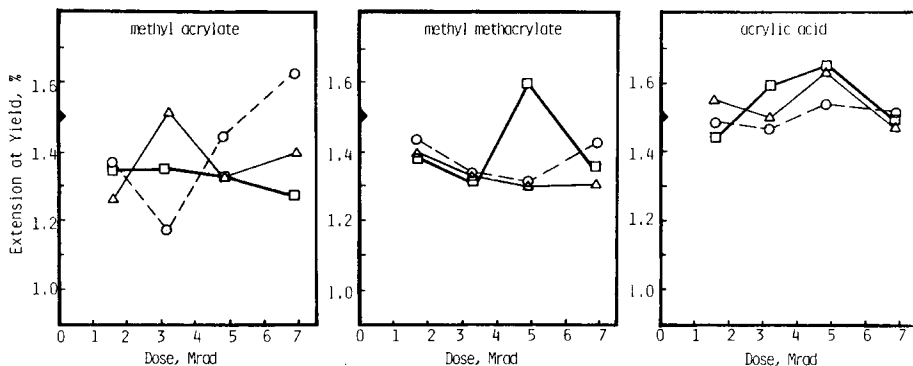


Fig. 2. Extension at yield of modified fibers: (○- -) 25°C; (△—) 60°C; (□—) 100°C; (◆) control.

changes, i.e., considerable increases in load at yield, in extension at break, and more pronounced decreases in load at break. In all these changes, the effect increased with dose till a maximum was reached at about 5 Mrad, dropping off again at 6 Mrad. A possible explanation is that crosslinks are forming at the higher dose.

In addition to these differences in stress-strain relationships, the fibers modified with AA had a softer hand, while the fibers modified with MA and MMA became harsher in hand. The melting temperature of the untreated PP film was 166°C determined by differential scanning calorimetry (DSC). The polymerization of AA was found not to affect the melting characteristics of the film. The degradation temperature determined by both DSC and thermal gravimetric analysis was found increased 10°–20°C for the AA-polymerized film.

CONCLUSIONS

The premonomer exchange mutual irradiation approach in this study was effective in enhancing polymerization of AA, MA, and MMA in the PP

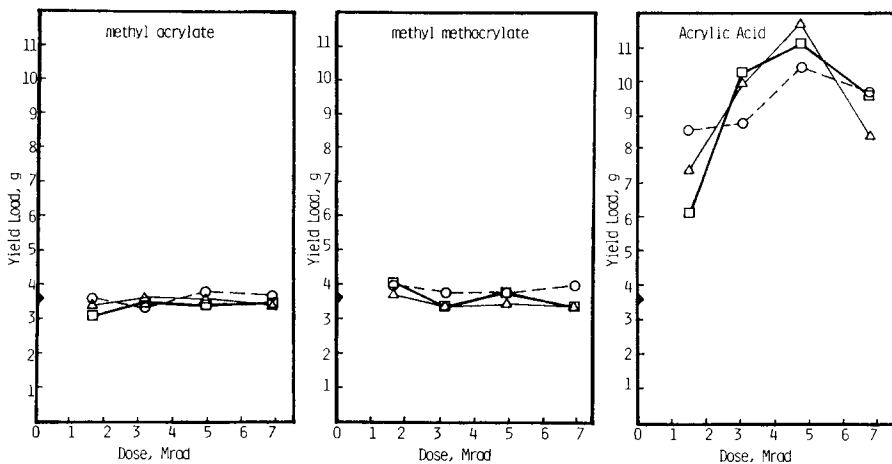


Fig. 3. Load at yield of modified fibers: (○- -) 25°C; (△—) 60°C; (□—) 100°C; (◆) control.

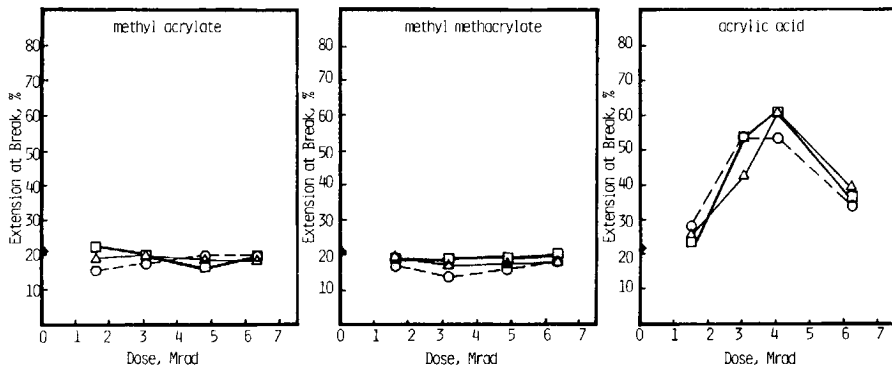


Fig. 4. Percent extension at break of modified fibers: (○ - -) 25°C; (△ —) 60°C; (□ —) 100°C; (◆) control.

substrates. Increase in polypropylene's hydrophilicity is primarily affected by the monomer used. Neither irradiation dose nor the use of swelling agent, i.e., *n*-butanol, were significant in producing similarly marked increases in surface wettability and moisture regain. Although the effects of other solvents as swelling agents could be studied in the future, this seems unnecessary considering the great improvements possible in polypropylene's hydrophilicity using no chemical pretreatments other than monomer exchange at a low γ -irradiation dose.

In addition to increasing wettability, methyl acrylate and methyl methacrylate modified polypropylene fibers have the advantage of no significant changes in strength or elongation. However, the resulting harsh hand is usually undesirable. Acrylic acid modified polypropylene fibers have the advantage of a softer hand and higher extension before breaking, but the disadvantage of a lower breaking strength.

References

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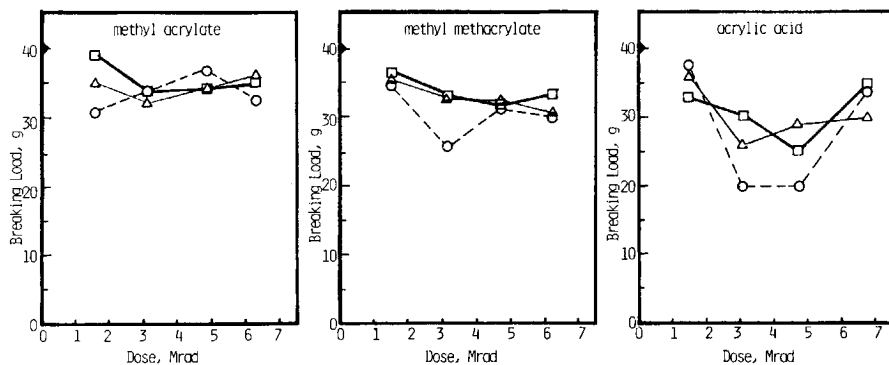


Fig. 5. Load at break of modified fibers: (○ - -) 25°C; (△ —) 60°C; (□ —) 100°C; (◆) control.

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