

Synthesis and Properties of Acrylonitrile-CR-Methyl Methacrylate Graft Copolymer

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SYNOPSIS

Graft copolymerization of acrylonitrile (AN) and methyl methacrylate (MMA) onto polychloroprene (CR) was carried out using benzoyl peroxide as initiator. The effects of mole ratio of AN to MMA, reaction temperature, reaction time, solvent, and initiator concentration on the graft copolymerization were examined. It was found that the thermal stability and weatherability of the AN-CR-MMA graft copolymer (ACM) were considerably better than those of CR.

INTRODUCTION

Polychloroprene (CR) is one of the most commonly used synthetic rubbers in adhesives and the transportation or energy industries because of its superior resistance to swelling in oil and its combination of polarity and crystallinity. A wide variety of types of CR is available to allow the users to formulate for their specific requirements. However, its poor heat resistance and weatherability limit the outdoor use of the material and its blends.^{1,2} Among the several attempts to improve the poor performances, the use of appropriate fillers for compounding has been widely investigated.³⁻⁵

Recently we reported on the synthesis and properties of acrylonitrile-ethylene-propylene-diene terpolymer (EPDM)-methyl methacrylate graft copolymer and concluded that the introduction of acrylonitrile (AN) and methyl methacrylate (MMA) can improve the light resistance, weatherability, and thermal stability of AN-butadiene-styrene (ABS) copolymer.⁶ The aim of this work is thus to improve heat resistance and weatherability of CR by grafting AN and MMA. AN and MMA were grafted onto CR under argon atmosphere in the presence of benzoyl peroxide (BPO) as an initiator. The effects of mole ratio of AN to MMA,

reaction temperature, reaction time, solvent, and initiator concentration were investigated in the graft copolymerizations. The thermal stability and weatherability of the graft copolymer were analyzed.

EXPERIMENTAL

Materials

CR (Denka Chemical, A90) having number-average molecular weight of 230,000 [M_w/M_n ; 2.4, determined by gel permeation chromatography (GPC; Waters 244)] was purified by the solution-precipitation technique; CR was first dissolved in toluene and then washed with methanol to extract out methanol-soluble additives. AN (Junsei Chemical) and MMA (Junsei Chemical) were purified by standard procedures. BPO (Hayashi Chemical) was recrystallized from methanol. Acetone, *n*-hexane, toluene, tetrahydrofuran (THF), ethyl acetate, and dimethyl formamide (DMF) were distilled prior to use.

Preparation of Materials

Synthesis of AN-CR-MMA Graft Copolymer (ACM)

Three grams of CR was dissolved in 100 mL of toluene. A mixture of AN and MMA at a given mole

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Table I Graft Copolymerization Conditions Used in This Study

Conditions	Description
Mole ratio of [AN]-[MMA]	0.1, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0
Polymerization time (h)	10, 20, 30, 40
Reaction Temperature (°C)	60, 70, 80, 90
Solvent	Toluene-THF = 100/0 75/25 50/50 25/75 0/100
Initiator concentration ($M \times 10^4$)	0.62, 1.24, 2.48, 4.95, 9.91

ratio was dissolved in 10 mL of toluene and then added with a given amount of BPO in a 1-L separable flask equipped with a modified Hopkins cooler. The

flask was sealed after charging with argon, and the reaction was carried out under various experimental conditions (see Table I).

After a chosen period of reaction, the contents were poured into methanol with stirring; the precipitate was filtered and dried under vacuum until a constant weight is reached. The nongrafted CR was extracted using ethyl acetate/*n*-hexane (6 : 7 v/v) mixed solvent. The ACM graft copolymer was isolated from a mixture of copolymer and homopolymers such as poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), and poly(AN-co-MMA) using acetone and DMF. The isolation procedure is shown schematically in Figure 1.

The structure of ACM was conformed by IR examination (Perkin-Elmer 1330). The IR spectra of ACM exhibited characteristic absorption bands at 2920 cm^{-1} (stretching vibration of aliphatic C—H bond), 2240 cm^{-1} (stretching vibration of C≡N group), 1720 cm^{-1} (stretching vibration of C=O group), 1650 cm^{-1} (stretching vibration of C=C

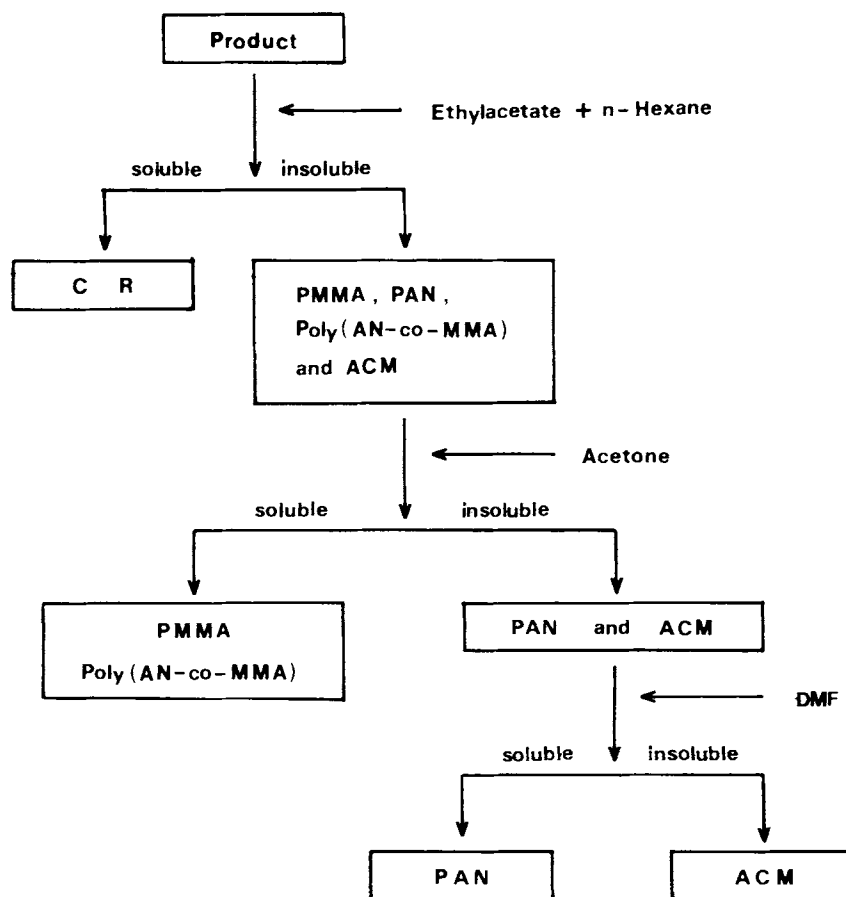


Figure 1 Block diagram of graft copolymer isolation process (Notations are described in the text).

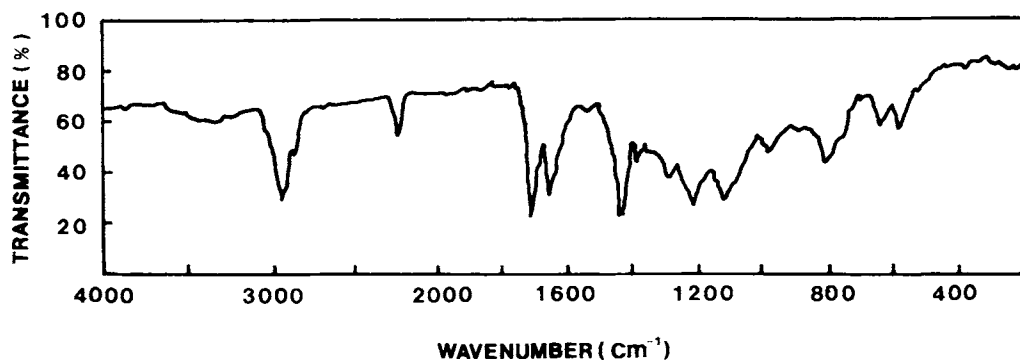


Figure 2 IR spectrum of acrylonitrile-CR-methyl methacrylate (ACM) graft copolymer.

bond), 1485 cm^{-1} (scissoring of CH_2), and 600 cm^{-1} (stretching vibration of C—Cl bond) (Fig. 2).

The total conversion, grafting ratio, and grafting efficiency of ACM were estimated by using the following equations⁷:

Total conversion (%)

$$= \frac{\text{total weight of crude product}}{\text{weight of monomer charged}} \times 100 \quad (1)$$

Grafting ratio (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{weight of substrate}} \times 100 \quad (2)$$

Grafting efficiency (%)

$$= \frac{\text{weight of polymer in grafts}}{\text{total weight of polymer formed}} \times 100 \quad (3)$$

Synthesis of Poly(AN-co-MMA)

Poly(AN-co-MMA) was prepared by reacting a mixture of 9.3 mL of AN and 5.0 mL of MMA dissolved in 70 mL of toluene with 0.06 g of BPO by the method described for preparation of ACM. The polymerization was carried out at 80°C for 30 h.

Measurements

Thermogravimetric analysis (TGA). Thermal stability was examined with a DuPont 1090 TGA instrument at a scanning rate of $15^\circ\text{C}/\text{min}$.

Weatherability. The weatherability (ASTM G53) was measured at 60°C , using a Q panel UV B313 Weathering Tester coupled with a UV lamp of 315–280 nm in wavelength. The film specimens were cast from THF solutions (ca. 3 wt %) on a nonyellowing urethane-coated hiding paper. The films were slowly dried at room temperature and then kept under vacuum until they reached constant

weight. The cross-sectional area of the films was $3 \times 5\text{ cm}^2$, and $35\text{ }\mu\text{m}$ thick. The weatherability was semiquantitatively expressed in terms of color difference (ΔE) with a National Bureau of Standards unit. The smaller ΔE means better weatherability.^{6,8} The samples were tested for 2 h in the Weatherometer for the measurements of weatherability. The color difference (ΔE) of the samples after exposing to UV and moisture was calculated using the Hunter-Schofield equation.^{9,10} A color difference meter (ND-101DP, Japan) was used for measurements of the color difference.

RESULTS AND DISCUSSION

Reaction Conditions

Effect of Mole Ratio

Figure 3 shows the effect of mole ratio of AN to MMA on the graft copolymerization onto CR. The

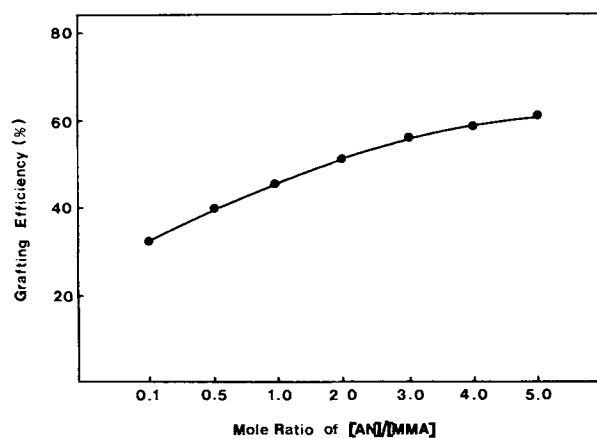


Figure 3 Plot of grafting efficiency vs. mole ratio of [AN] to [MMA]: reaction temp., 80°C ; reaction time, 30 h; solvent, toluene; BPO, 0.06 g.

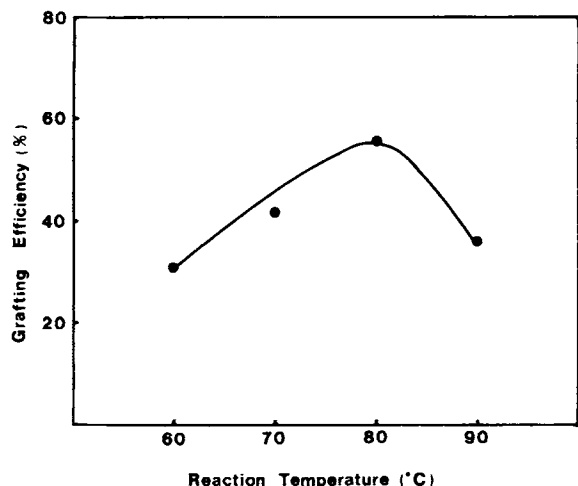


Figure 4 Plot of grafting efficiency vs. reaction temperature: [AN]–[MMA], 3.0; reaction time, 30 h; solvent, toluene; BPO, 0.06 g.

reaction was carried out in toluene with 0.06 g of BPO as an initiator at 80°C for 30 h.

It can be seen that the grafting efficiency increases with increasing mole ratio of AN to MMA up to 3.0, but thereafter it levels off. This effect may be explained by considering the difference in reactivity between AN and MMA; r_1 of AN and r_2 of MMA were reported as 0.13 and 1.16, respectively, for the copolymerization, meaning that AN has much lower tendency to homopolymerize than MMA.^{6,11} The leveling of the curve is probably caused by the combined effects of decreasing concentration of the unreacted monomers as reaction proceeds and increasing viscosity of the system because of the increasing concentration of polymer formed by reaction.

Effect of Reaction Temperature

The highest grafting efficiency was observed at 80°C within our experimental temperature ranges, as shown in Figure 4. It may be related to the decomposition rate of BPO as a function of temperature.^{12,13} The grafting was carried out with a constant BPO content (0.06 g) and a fixed mole ratio of AN to MMA at 3.0 for 30 h.

Effect of Reaction Time

The effect of reaction time on the graft copolymerization is shown in Figure 5. The grafting was carried out at constant BPO content (0.06 g) at 80°C. The mole ratio of AN to MMA was fixed at 3.0. The grafting efficiency increased with reaction time up

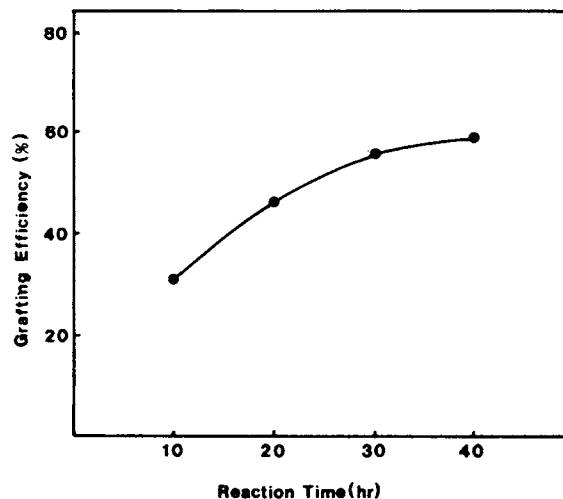


Figure 5 Plot of grafting efficiency vs. reaction time: [AN]–[MMA], 3.0; reaction temp., 80°C; solvent, toluene; BPO, 0.06 g.

to 30 h and then leveled off. This may be also caused by the decrease of the unreacted monomer concentrations as well as the increase of viscosity of the reaction mass along the reaction path.

Effect of Solvent

Figure 6 shows the effect of solvent on the graft copolymerization. The reaction was carried out with 3.0 mole ratio of AN to MMA and 0.06 g of BPO at 80°C for 30 h. The grafting efficiency is highest at

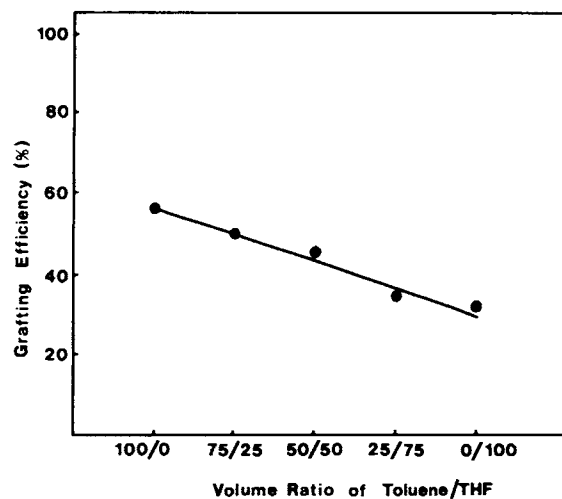


Figure 6 Plot of grafting efficiency vs. solvent: [AN]–[MMA], 3.0; reaction temp., 80°C; reaction time, 30 h; BPO, 0.06 g.

Table II Effect of Initiator Concentration on the Graft Copolymerization of AN and MMA onto CR^a

Initiator Concentration ($M \times 10^4$)	Total Conversion (%)	Grafting Ratio (%)	Grafting Efficiency (%)
0.62	38	63	33
1.24	51	177	45
2.48	61	182	56
4.95	82	333	53
9.91	92	356	51

^a [AN]-[MMA] = 3.0, reaction temp. = 80°C, reaction time = 30 h, solvent = toluene.

56% when toluene was used as solvent whereas the grafting efficiency is decreased with increasing composition of THF in the toluene-THF mixed solvents. These results come from the difference in solvent power of each solvent-polymer pair^{14,15}; i.e., THF is a good solvent for CR but a poor solvent for ACM or other copolymers and homopolymers obtained as by-products such as poly(AN-co-MMA), respectively, whereas toluene is a good solvent for both CR and ACM. Thus, it was found that, since toluene dissolves the polymers more readily than THF, the grafting efficiency was the highest when toluene was used as a solvent. Odian et al. reported similar results of solvent effect on graft copolymerizations of styrene onto nylon, polyethylene, and polypropylene.¹⁶⁻¹⁸ The result was also in accordance with our previous results on the AN-EPDM-MMA copolymer.⁶

Effect of Initiator Concentration

The effect of initiator concentration on the graft copolymerization is shown in Table II and Figure 7. The reaction conditions were the same as those described above. The grafting efficiency showed a maximum at the concentration of $2.48 \times 10^{-4} M$ whereas the total conversion and the grafting ratio were increased with increasing initiator concentration. This result is expected since the homopolymer or poly(AN-co-MMA) are formed more readily than the graft copolymer at higher initiator concentration.

Thermal Stability

The effect of mole ratio of AN to MMA on the thermal stability is shown in Figure 8. The decomposi-

tion temperature increases as the mole ratio increases. Final decomposition temperature of ACM having mole ratio of 1.0 is 355°C and those of ACM having mole ratio of 5.0 is 483°C. The trend is ascribed to the flame-retardant role of AN. This speculation is supported by the fact that the residual weight after decomposition at 500°C for the ACM having mole ratio of 5.0 (40%) is much higher than that for the ACM having mole ratio of 1.0 (20%). Tang and Niell¹⁹ and Nara and Matsuyama²⁰ reported in their separate studies on α -cellulose or epoxy resins that the material having more residues after decomposition has better flame retardance.

The effect of reaction temperature in graft copolymerization on the decomposition temperature is shown in Figure 9. The ACM synthesized at 80°C

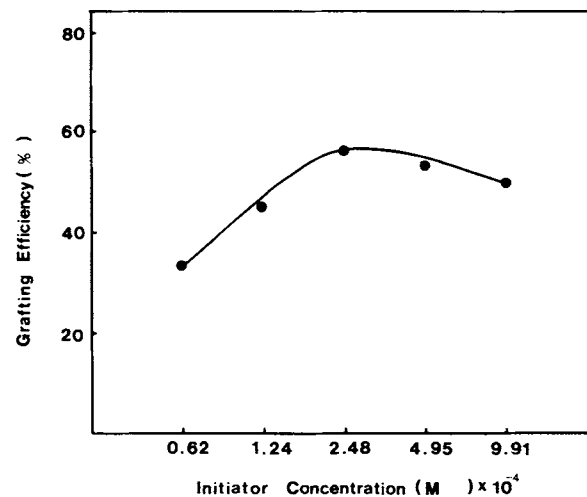


Figure 7 Plot of grafting efficiency vs. initiator concentration; [AN]-[MMA], 3.0; reaction temp., 80°C; reaction time, 30 h; solvent, toluene.

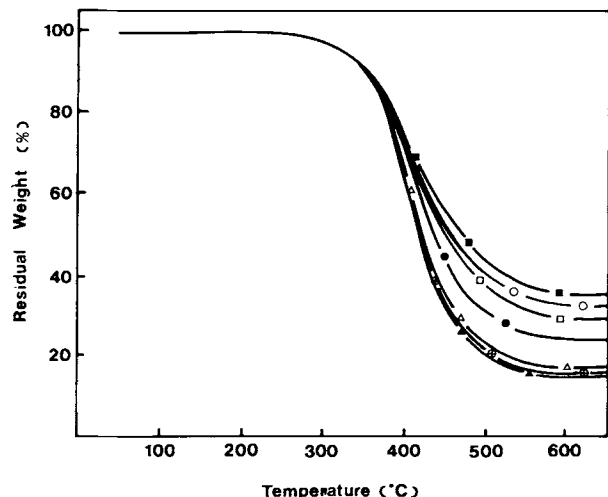


Figure 8 Effect of mole ratio of AN to MMA in graft copolymerization of ACM on the TGA curves; heating rate, 15°C/min in air: ([AN]-[MMA]: -▲-, 0.1; -⊕-, 0.5; -△-, 1.0; -●-, 2.0; -□-, 3.0; -○-, 4.0; -■-, 5.0).

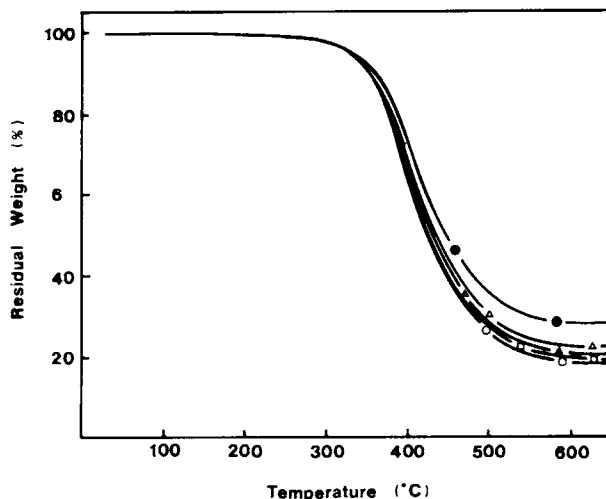


Figure 10 Effect of solvent in graft copolymerization of ACM on the TGA curves; heating rate, 15°C/min in air: (-●-, toluene; -△-, toluene-THF (75/25); -▲-, toluene-THF (50/50); -□-, toluene-THF (25/75); -○-, THF).

showed the highest final decomposition temperature, viz. 458°C. The result may be related to the highest grafting efficiency at the reaction temperature due to the decomposition rate of BPO as a function of temperature. Similar behavior was also observed for ACM having different reaction time and initiator concentration, but the effect of the reaction condi-

tions on the thermal stability were not significant in our experimental ranges.

The influence of solvent in graft copolymerization on the decomposition temperature should be also noted, as shown in Figure 10. The ACM synthesized in toluene showed highest final decomposition temperature but ACMs synthesized in THF or toluene-

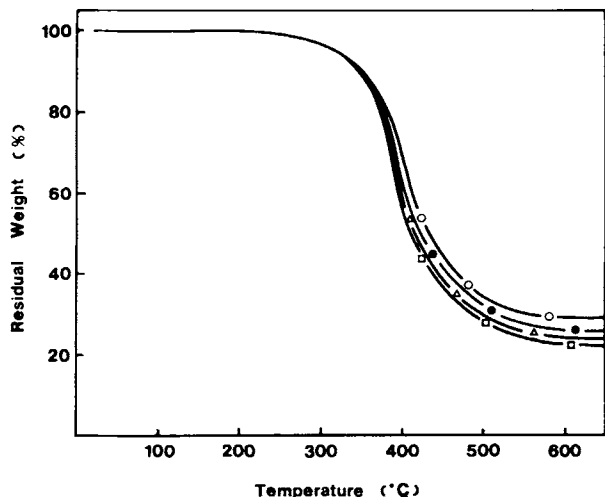


Figure 9 Effect of reaction temperature in graft copolymerization of ACM on the TGA curves; heating rate, 15°C/min in air: (-□-, 60°C; -△-, 70°C; -○-, 80°C; -●-, 90°C).

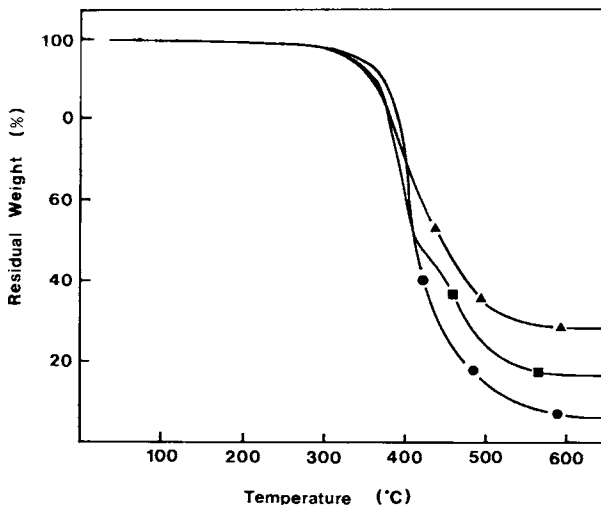


Figure 11 TGA curves of various samples; heating rate, 15°C/min in air: [-▲-, ACM; -■-, CR; -●-, poly(AN-co-MMA)].

Table III Decomposition Temperature and Percent Weight Residue of Various Samples

Samples	Initial Decomposition Temperature (°C)	Weight Residue at 500°C (%)
CR	362	24
poly(AN-co-MMA)	383	15
ACM	369	35

THF mixed solvents showed lower decomposition temperature as the volume percent of toluene decreased in the mixed solvents. This may be due to the difference in solvent power. Note that the grafting efficiency becomes higher in better solvent.

Figure 11 shows TGA curves of ACM, poly(AN-co-MMA), and CR. It is clear that the ACM shows superior thermal stability with highest thermal decomposition temperature. As shown in Figure 11 and Table III, the residual weight at 500°C is 35% whereas those of other polymers are 24 and 15% for CR and poly(AN-co-MMA), respectively. The thermal stability of ACM may be attributed to the synergistic effect of the chlorine atom in CR and flame-retardant role of AN. The ACM referred to in Figure 11 was synthesized with 3.0 mole ratio of

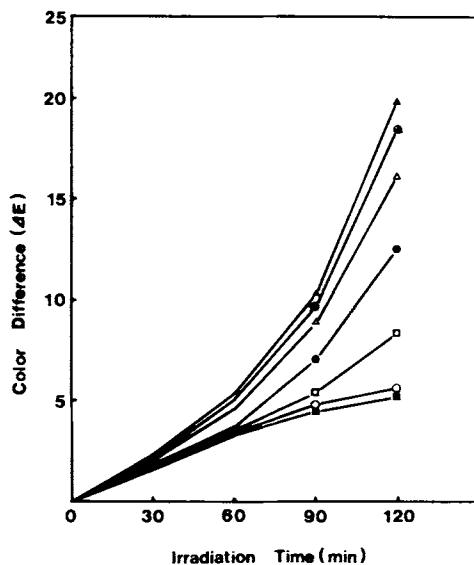


Figure 12 Effect of mole ratio on the plot of color difference vs. irradiation time ([AN]-[MMA]: -▲-, 0.1; -⊕-, 0.5; -△-, 1.0; -●-, 2.0; -□-, 3.0; -○-, 4.0; -■-, 5.0).

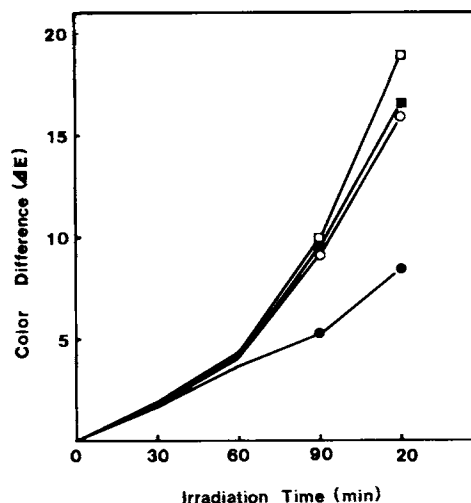


Figure 13 Effect of reaction temperature on the plot of color difference vs. irradiation time (-□-, 60°C; -■-, 70°C; -●-, 80°C; -○-, 90°C).

AN to MMA and 0.06 g of BPO at 80°C for 30 h in toluene.

Weatherability

The effect of mole ratio of AN to MMA on the weatherability is shown in Figure 12. The ACM with higher mole ratio revealed better weatherability. However, the improvement of weatherability with

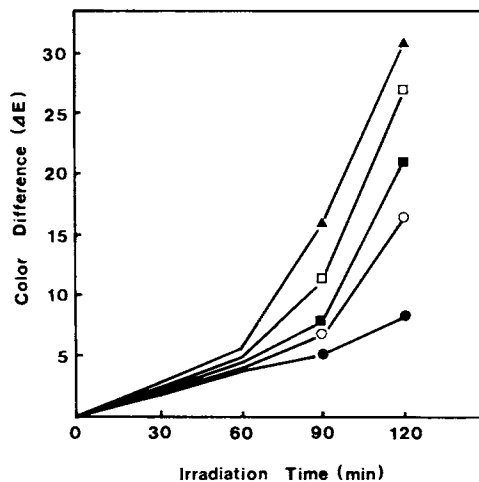


Figure 14 Effect of solvent on the plot of color difference vs. irradiation time (-●-, toluene; -○-, toluene-THF (75/25); -■-, toluene-THF (50/50); -□-, toluene-THF (25/75); -▲-, THF).

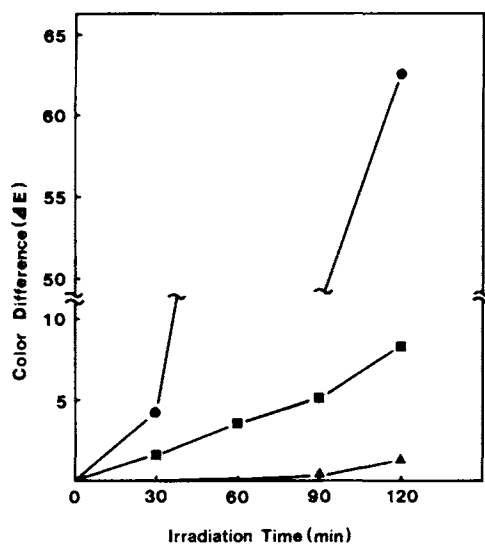


Figure 15 Plot of color difference vs. irradiation time for various samples. [—●—, CR; —■—, ACM; —▲—, poly(AN-co-MMA)].

increasing mole ratio becomes weaker above the mole ratio of 3.0. The result is related with the leveling in the grafting efficiency as a function of mole ratio, which was already discussed in the previous section. The dependencies of weatherability of ACM on the reaction temperature and solvent are illustrated in Figures 13 and 14.

The ACM synthesized at 80°C showed lowest color difference and thus best weatherability (Figure 13). The influence of solvent in graft copolymerization on the weatherability should be also noted, as shown in Figure 14. The ACM synthesized in toluene showed best weatherability whereas ACMs synthesized in THF or toluene-THF mixed solvents showed poorer weatherability as the volume percent of toluene decreased in the mixed solvents. These results may be related to the influence of the reaction conditions on the grafting efficiency. It was observed that the effect of reaction time and initiator concentration on the weatherability were not significant in our experimental ranges.

It should be noted that the ACM shows much better weatherability than CR, even though a poly(AN-co-MMA) shows better weatherability than ACM (see Fig. 15). This result implies that the incorporation of AN and MMA are very effective to improve poor weatherability of CR. The grafted ACM was synthesized in toluene with 3.0 mole ratio of AN to MMA and 0.06 g of BPO at 80°C for 30 h.

CONCLUSIONS

AN-CR-MMA graft copolymer (ACM) was synthesized with radical initiator by the solution polymerization technique. The dependence of material properties on the various reaction conditions was investigated. The important results are summarized as follows:

1. In the graft copolymerization of ACM, the grafting efficiency increased with increasing AN content relative to that of MMA up to 3.0, then leveled off.
2. The grafting efficiency was highest at 80°C when toluene was used as solvent.
3. The grafting efficiency was highest at the BPO concentration of 2.48×10^{-4} M.
4. The grafting efficiency of ACM increased up to 30 h, then leveled off.
5. The thermal stability of ACM increased with increasing mole ratio of AN to MMA and showed a maximum for the ACM synthesized at 80°C when toluene was used as a solvent.
6. The thermal stability of ACM was better than that of CR.
7. The weatherability of ACM was improved as the mole ratio AN to MMA increased and showed a maximum for the ACM synthesized at 80°C when toluene was used as a solvent.
8. The weatherability of ACM was significantly enhanced as compared to CR.

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