

The electron-beam (EB) irradiation and grafting of acrylic monomers onto EPDM copolymer

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Abstract Radiation techniques (electron-beam, γ -ray, etc.) are usually used for improving the compatibility between polymer and ingredients in composite materials. Electron-beam pre-irradiation has been used for the first time to enhance the flame retardance of EVA copolymer. Efforts are being made to decline the flammability for EPDM copolymer by EB technique and remarkable reduction has been attained through a series of treatments: pre-irradiation, grafting and saponification.

Keywords: electron-beam grafting, flame retardance, EPDM.

1 Experimental

The EPDM1040 was firstly pressed by a two-roll mixing mill and then reduced to specimens for test. Thermal Gravimetric Analysis (TGA) and Cone calorimeter were employed to characterize the flammability of grafted specimens^[1,2].

2 Factors affecting grafting yield

(i) Time of irradiation. Experiments were performed under the following conditions: thickness of specimens: 0.3 mm, concentration of monomers: 10%, reaction time: 2 h, reaction temperature: 98°C. Fig. 1 gives grafting yields for three monomers as the functions of irradiation time. The sequence of activity for monomers is MAA > AAm > AA. The maximum weight percent of Gr for MAA is attained at 1 000 s, but little difference in the initial stage has been found between AAm and AA. Grafting reactions could hardly continue if the specimens were laid for a long time, and should be conducted within an appropriate period of time due to the unstable peroxide radicals generated in EPDM matrix by irradiation. The reason may be the formation of hydrogen atoms which may further lead to the creation of H₂O₂. It is known that hydrogen peroxide is more unstable than the peroxides^[3].

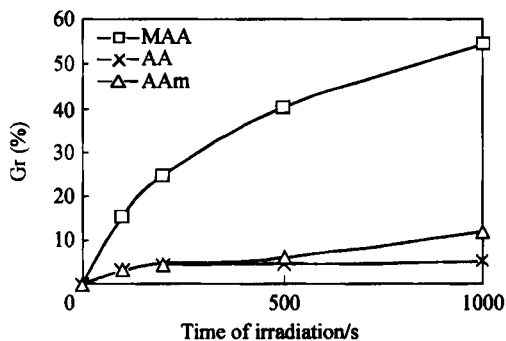


Fig. 1. Change in grafting yield vs. time of irradiation.

(ii) Time of grafting. Experiments were performed under the following conditions: 0.3 mm thickness, 500 s irradiation time, 10% monomer concentration, and temperature 98°C. Similar curves can be seen in fig. 2. The higher the concentration of monomer used in the grafting solution, the greater the density of radicals generated in the EPDM matrix. The grafting yield thus grows as reaction time increases.

(iii) Monomer concentration. Experiments were performed under the following conditions:

Abbreviations and nomenclatures: MAA, methyl acrylic acid; AA, acrylic acid; AAm, acrylic amide; Gr, grafting yield. For g-X (Y,Z%): g, grafting; X, polymer to be grafted; Y, graft monomer; Z%, grafting yield; THE, total heat release; HE_(av), heat evolved per unit mass; HRR_(av), average heat release rate; HRR_(peak), peak heat release rate; EHC_(av), average efficient heat of combustion; SEA_(av), average specific extinguishment area.

thickness: 0.3 mm, reaction time: 2h, temperature: 98°C. Quite similar curves for the grafting yield of EPDM as the function of MAA concentration can also be seen in fig. 3. Experimental data of polyethylene and polypropylene are also depicted in the figure. These results can be explained in terms of Chaudles' formula^[3], namely, at the same dose rate I and reaction time t , the different grafting yield resulting from different F (diffusion factor), Φ_p (molar yield of radicals), K_t (chain-growing constant) and K_p (termination constant).

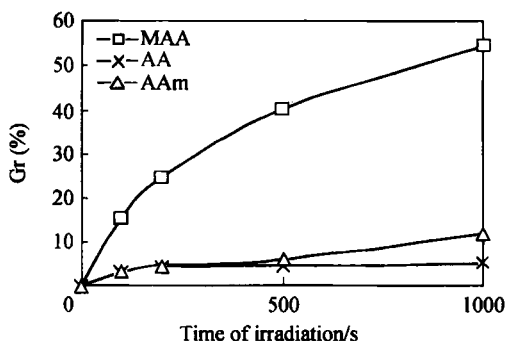


Fig. 2. Change in grafting yield vs. time of grafting reaction.

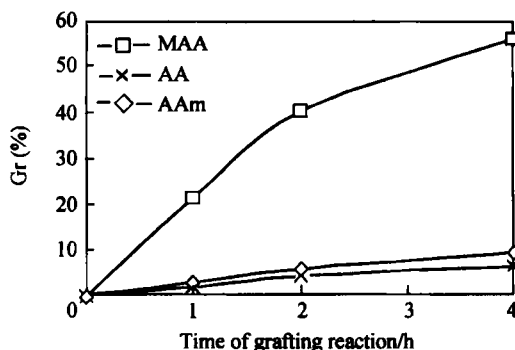


Fig. 3. Change in grafting yield vs. concentration of monomer MMA.

3 Characterizing the flame retardance of grafted specimens

(i) TTI method. Using comprehensive vertical burning tester, the TTI was measured for grafted specimens as given in table 1. For details see refs.[1, 2]. TTI for all grafted specimens are all extended. It can be dramatically extended after treatment by saponification. The higher the graft yield attained, the larger the difference in resulting TTI. For example, the difference Δ TTI was 32.8 s at the grafting yield of 54.2 relative to that before saponification.

Table 1 TTI of grafted EPDM at different grafting yield

Gr (MAA)(%)	Before saponification/s	After saponification/s	Gr (AA)(%)	TTI/s	Gr (AAm)(%)	TTI/s
0.0	3.0	3.0	0.0	3.0	0.0	3.0
6.1	5.0	11.7	3.2	3.2	1.4	5.0
11.7	6.2	16.9	4.3	4.3	4.0	9.5
40.2	12.1	26.5	4.5	4.6	6.0	16.6
54.2	13.2	35.8	4.9	5.1	11.6	24.1

(ii) Cone calorimetry. Experimental conditions: thickness 1 mm; sample area 70 mm × 70 mm; irradiation power 25 kW/m²; gas flow rate 30 L/s.

TTI data from Cone below show quite a similar trend to that tested from the comprehensive vertical burning tester, implying the validity of technical approach through EB irradiation followed by grafting and saponification. From our TGA data (omitted for simplicity) one can see that the EPDM before grafting gives no char residue at all at 500°C. However, after grafting, especially with saponification the char residues of the specimens increase quickly, indicating that the fore-mentioned technique is really effective in catalyzing char formation, which is of great significance to prevent the polymer substrate underlying the surface from mass and heat transfer into the bulk.

While searching for the difference of TTI between un-irradiated and irradiated EPDM, we found that the irradiated EPDM appeared to be slightly longer by 5 s than the un-irradiated specimens. It clearly suggested that the cross-linking predominated in the process slightly over the chain scission which occurred simultaneously with cross-linking. In short, a number of parameters of grafted EPDM, such as HRR_(av), HRR_(peak), EHC and SEA are all improved compared with those of the origins. Reduction of HRR and SEA must then impart valuable flame retardance to EPDM (see table 2).

(iii) Characterization of thermal behavior and charring by TGA. Wilkie et al.^[4] reported that the TGA curve of poly(methacrylic acid) offered a residue of 5%; nonetheless, after treatment by NaOH,

NOTES

Table 2 Some Cone data of grafted EPDM

Sample	TI/s	THE/kJ	HE _(av) /kJ · g ⁻¹	HRR _(av) /kW · m ⁻²	HRR _(peak) /kW · m ⁻²	EHC _(av) /MJ · kg ⁻¹	SEA _(av) /m ² · kg ⁻¹
EPDM	52	223.2	45.6	185.3	1 269.7	48.3	584.1
Irradiation (100 s)	57	225.1	44.7	178.9	1 243.8	45.6	577.9
g-EPDM(AAm, 2.2%) (500 s/L)	69	220.3	44.2	151.5	884.9	41.7	556.2
g-EPDM(AAm, 2.0%) (500 s/L)	69	221.3	43.9	150.2	965.6	41.4	562.1
g-EPDM(AAm, 2.3%) (500 s/L)	65	216.2	44.0	175.7	1 197.0	38.5	589.3
g-EPDM(AAm, 0.8%) (100 s/L)	61	226.8	43.2	176.2	1 203.8	38.7	551.4
g-EPDM(AAm, 5.2%) (500 s/L)	78	209.6	41.5	167.5	1 076.1	36.7	552.0
g-EPDM(AAm, 5.6%, 1 h) (500 s/L)	106	185.4	35.3	128.2	932.9	35.0	495.7

the residue develops easily up to 13%. Based on such analysis, theoretical char residue can be calculated. For instance, the grafting yield by MAA onto a polymer is assumed to be 10%; the deposited substance (grafting) is then about $10/110 = 9.1\%$. Therefore, the theoretical char residue ought to be $5\% \times 9.1\% = 0.46\%$. Charring should thus be considered realized, if the residue taken from TGA shows a value greater than 0.46%. The same is true for specimens after treatment by NaOH. At grafting yield of 10% MAA the theoretical char residue should be $13\% \times 9.1\% = 1.18\%$. Charring should also be considered realized, if the residue taken from TGA shows a value greater than 1.18%. We have measured the char residues for monomer (AAm), oligomers (AAm and AA) and polymers (MAA, NaMAA, and AAm) by TGA (see table 3).

Table 3 Char residues measured for monomer, oligomers and polymers by TGA

Sample	MAA (polymer)	NaMAA (polymer)	AA (oligomers)	AAm (monomer)	AAm (polymer)	AAm (polymer)
Char residue (%)	5.0	13.0	5.4	8.9	10.0	25.0

Experiments show that AAm itself appears to be a good char-former. Its capability of forming char at 600°C depends much on its degree of polymerization. It is reasonable that theoretical calculations should be conducted on oligomers, because during grafting the grafted monomer onto substrate polymer existed mostly in a state of oligomer.

From tables 4 and 5 it can be seen that:

(i) Corresponding to the chain scission, only one peak could be observed in TG thermographs for the control sample, g-EPDM(MAA), g-EPDM(AA), g-EPDM(AAm). Where two peaks were found for g-EPDM(MAA) followed by saponification, which correspond to side chain and main chain scission, respectively. (ii) The mass loss rate of samples at maximum after grafting was evidently smaller than those before treatment. (iii) The T_{onset} of mass loss appeared earlier through grafting. (iv) Dramatic changes took place in char residue after grafting. The increase in char yield depends significantly on the grafting yield. Of vital importance is the saponification which should be invoked in catalyzing char formation.

Table 4 Some TGA data of grafted EPDM

Sample	Peak No.	Onset temperature of degradation /°C	Ultimate temperature at plateau/°C	Maximal rate of mass loss /(% · °C ⁻¹)	Temperature at maximal rate of mass loss/°C
EPDM	1	415.17	499.80	2.729	479.61
g-EPDM (AA, 5%)	1	388.95	501.45	2.216	471.16
g-EPDM (AAm, 2%)	1	410.39	499.81	2.707	476.73
g-EPDM (MAA, 15%)	1	397.63	504.36	1.887	474.07
g-EPDM (MAA, 36%)	1	365.88	498.57	1.780	472.61
g-EPDM (MAA, 32%, 1 h)	1	380.20	498.47	1.789	475.39

Table 5 Calculated and experimental char residues of grafted EPDM (TGA)

Sample	Calculated char residues (%)	Experimental char residues (%)
EPDM	0.00	0.00
g-EPDM(AA, 5%)	0.25	0.00
g-EPDM(AAm, 5%)	0.20	0.00
g-EPDM(MAA, 15%)	0.65	1.80
g-EPDM(MAA, 36%)	1.32	3.47
g-EPDM(MAA, 32%, 1 h)	3.15	6.22

4 Conclusions

The pre-irradiated EPDM by EB ought to be dealt with in grafting within a short period of time, because the concentration of peroxide radicals decays quickly.

It is practical to render the grafting yield higher through extending the time of irradiation and grafting and increasing the concentration of monomers as well.

The improvement of flame retardant EPDM by EB-induced grafting and/or saponification is mirrored in the increase of LOI and char residue, and the decrease of HRR, SEA, THE and so on.

EB-induced grafting plus metallic ions manifest themselves as a potential approach which may impart flame retardance to polymers, even though it is modified within surface layers. It provides a new route for non-halogen flame retardant materials with a minor influence on the properties of bulk polymers.

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