Radiation Grafting of Methyl Methacrylate Monomer on Natural Rubber Latex

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Synopsis

A method of radiation grafting of methyl methacrylate (MMA) monomer on natural rubber (NR) latex has been studied. The irradiation dose in radiation emulsion polymerization of MMA monomer was lower compared to the irradiation dose for grafting of MMA monomer on NR latex, in order to obtain the same degree of conversion. This is due to the size of the rubber particles which are quite large and, hence, not sufficient to ensure an ideal emulsion polymerization. The irradiation dose for radiation grafting of MMA monomer on latex was around 300 krad to obtain a 75% degree of conversion. However, this irradiation dose was lower compared to the irradiation dose for bulk polymerization of MMA monomer, in order to obtain the same degree of conversion. This is due to the gel effect in the viscous media. Radiation grafting of MMA monomer on NR latex does not influence the pH of the latex, but influences the viscosity significantly. The viscosity of the NR latex increased with an increase in irradiation dose, due to the increase of the total solid content in the latex. The MMA monomer converted to P-MMA in NR latex was largely grafted on the NR, or at least insoluble in a solvent for P-MMA, such as acetone or toluene. The hardness of the pure gum vulcanizate increased with an increase in the degree of grafting or P-MMA content, but the other physical properties, such as tensile strength, modulus, elongation at break, and thermal stability, were not greatly influenced by the degree of grafting.

INTRODUCTION

Heveaplus MG or NR–MMA copolymer is one of the grafted natural rubbers which has been used commercially. The major use for Heveaplus is in the field of adhesives.[1] Heveaplus MG has been produced commercially using a conventional method with hydroperoxide–polyamine as an initiator. The film forming properties of NR–MMA prepared by this method were poor, because the grafting reaction occurred largely on the surface of the rubber particles. This is true if the initiator used for the grafting reaction is a water-soluble initiator. The NR–MMA prepared by radiation grafting is expected to have better film homogeneity compared to the film prepared by a conventional method because the radicals which initiate the grafting reaction are produced in the entire inner mass of the particles.[2]

Research in this field to date, has yielded insufficient results to meet the needs of a commercial application.[3,4] This paper presents the experimental results and the physical properties of the film or latex. The purpose of this study is to get information relating to the preparation and properties of NR–MMA such as thermal stability, tensile strength, hardness, etc. This study is limited to the application of gamma radiation for the grafting processes.

EXPERIMENTAL

Materials. Concentrated rubber latex was obtained from Pasir Waringin

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TABLE I
Grafting of MMA on Natural Rubber: Influence of Irradiation Dose on the MMA Conversion

Irradiation dose (krad)	Conversion (%) Addition of MMA (10.7 phr)	Addition of MMA (21.4 phr)	Addition of MMA (32.0 phr)
25	3.10	5.25	11.42
50	12.86	22.72	27.54
75	25.37	35.79	34.18
100	36.45	46.24	56.20
200	62.90	67.89	71.10
300	72.36	75.79	77.37

Estate, West Java, Indonesia. The dry rubber content of the mentioned latex was about 60% and the viscosity was about 50 cP. The latex was diluted with a solution of ammonia to decrease the viscosity and increase the stability. MMA monomer was purified by distillation under reduced pressure. Other chemicals were analytical grade and were used without further purification.

Equipment. Irradiation was carried out using a Panoramic Co-60 Irradiator, 55 kCi activity. A Fricke dosimeter was used to calibrate the irradiation dose rate. An Instron Tensile Strength Tester, Model 1122, was used to determine the physical strength of the vulcanizates, and a Shimadzu Thermal Analyzer DT-30 was used to determine the thermal stability of grafted rubber.

Sample Preparation. A concentrated natural rubber latex sample, of about 60% dry rubber content, diluted with a dilute ammonia solution (1.5%), decreases the dry rubber content of the latex to 50%. The purpose of the dilution is to reduce the viscosity and, hence, stabilize the latex during irradiation. The diluted natural rubber latex was then mixed with a given amount of MMA monomer to which a small amount of Tween 20 has been added as an emulsifier. The mixture was stirred slowly by an electric stirrer for about 2 h, stored overnight and then irradiated. Irradiation was carried out at a dose rate of about 100 krad/h. Irradiation doses were 25, 50, 75, 100, 200, and 300 krad. The viscosity, pH, solid content, and the degree of conversion were determined just after irradiation.

Degree of Grafting and Conversion. The degree of conversion of MMA monomer to polymer was determined gravimetrically. The degree of grafting was determined as follows: irradiated latex samples were mixed with a dispersion of 2 phr sulfur, 2 phr ZnO, 2 phr ZDC, and 0.2 phr pepsin. The mixture was poured on a glass plate and dried. The dried film was heated at 100°C for about 60 min to obtain a pure gum of rubber vulcanizate. The vulcanizate was extracted by using acetone or toluene solvent to remove the P-MMA and any soluble matter. Extraction was carried out using a Soxhlet apparatus for about 70 h. P-MMA homopolymer is soluble either in acetone or toluene solvent, but the grafted natural rubber is unsoluble in the mentioned solvents. The degree of grafting was determined by the assumption that the unextracted P-MMA is the grafted polymer.

Physical Testing. The physical properties of the vulcanizates were determined according to ASTM. The activation energy of thermal degradation, E_a, was determined using Osawa equation as follows:

$$E_a = \frac{RT_1T_2 \log \beta_2/\beta_1}{0.457(T_1 - T_2)}$$

TABLE II
Average Activation Energy of Thermal Degradation for Grafted Natural Rubber (NR–MMA), at Conversion between 10% and 70% Calculated Using the Osawa Equation

Materials	Activation energy E_a (kcal/mol)
1. P-MMA	25.57 ± 5.05
2. Natural rubber, NR	51.67 ± 4.02
3. NR–MMA, 5% degree of grafting	54.59 ± 6.75
4. NR–MMA, 10% degree of grafting	52.78 ± 6.92
5. NR–MMA, 15% degree of grafting	61.19 ± 12.58
6. NR–MMA, 21% degree of grafting	56.14 ± 6.02

where E_a = activation energy of thermal degradation (cal/mol), T_1 = degradation temperature (°K) at the heating rate of β_1 and the degree of conversion, C, T_2 = degradation temperature (°K) at the heating rate of β_2 and the degree of conversion, C, and R = gas constant, 1.987 cal/mol·°K.

RESULTS AND DISCUSSION

Irradiation Dose. The influence of irradiation dose on the degree of conversion can be seen in Table I. The degree of conversion increases with the increase in irradiation dose, and at the irradiation dose of about 300 krad, the degree of conversion attains 75%. The degree of conversion also depends on the monomer concentration in the latex particles, which may be due to the difference in reaction efficiency.

The irradiation dose needed to graft MMA monomer on NR latex was much higher compared to the irradiation dose needed to obtain the same degree of conversion in the emulsion polymerization of MMA monomer, at the same irradiation dose rate. The irradiation dose needed to obtain a 70% degree of conversion of the emulsion polymerization of MMA monomer was less than 100 krad, at a dose rate of around 100 krad/h.[5] This is due to the size of the rubber particles, which are quite large and, hence, not sufficient to ensure ideal emulsion polymerization, as stated in the Smith–Ewart rate theory.[6] However, the irradiation dose for grafting is much lower compared to the irradiation dose of bulk polymerization at the same dose rate needed to obtain the same degree of conversion, as computed by the following equation:

$$C = 100(1 - e^{-k_p(R_i/k_t)^{1/2}t})$$

where C = degree of conversion (%), k_p = rate constant for propagation, 410 L/mol·s for MMA monomer, k_t = rate constant for termination, 24.1×10^6 L/mol·s, for MMA monomer, R_i = rate of radical production, 2.8×10^{-8} mol/L·s at 100 krad/h irradiation dose rate, and t = irradiation time (s).[7] Based on that equation, it can be computed that, for bulk polymerization of MMA monomer, the irradiation dose needed to obtain the 75% degree of conversion is about 1.23 Mrad. This irradiation dose is much higher compared to the one needed for the grafting reaction, which may be due to the gel effect of the grafting reaction in the viscous media.

Thermal Stability. Figures 1, 2, and 3 show the thermograms of NR, P-MMA, and NR–MMA. The heating rate influences the displacement distance

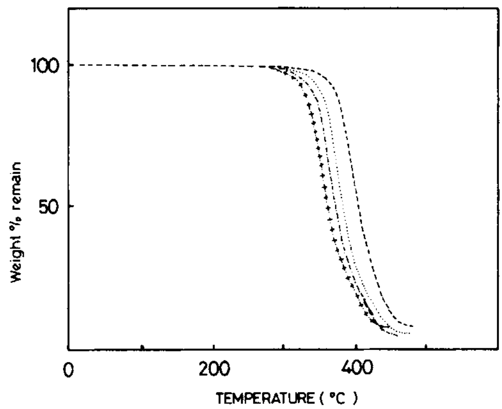

Fig. 1. Thermogram of natural rubber (NR). Influence of heating rate (°C/min): (+·+) 2; (-·-) 5; (· · ·) 10; (- - -) 30. E_a calcd: 51.67 ± 4.0 kcal/mol.

of the thermograms. The distance of displacement depends on the thermal stability of the polymer. Based on the distance of displacement, the activation energy E_a, for thermal degradation, can be calculated using the Osawa equation. Table II shows the activation energy E_a of grafted natural rubber, NR–MMA. E_a did not differ greatly between the grafted NR and the ungrafted one, although the activation energy for P-MMA is much lower compared to NR. The activation energy of P-MMA was 25.57 ± 5.05 kcal/mol, compared to NR which was 51.67 ± 4.0 kcal/mol. By comparison the activation energy for thermal degradation NR–MMA at 10% degree of grafting was 52.78 ± 6.92 kcal/mol. Under certain conditions, radiation grafting of MMA monomer on NR latex does not significantly influence its thermal stability.

Viscosity. Table III shows that irradiation does not influence the pH of the latex, but clearly influences the viscosity. The viscosity of NR latex increased with the increase in irradiation dose, which may be due to the increase in the total solid content of the latex. As a comparison, the viscosity of a concentrated NR (60% total solid) was 55 cP, the diluted latex (50% total solid) was 15 cP, and the

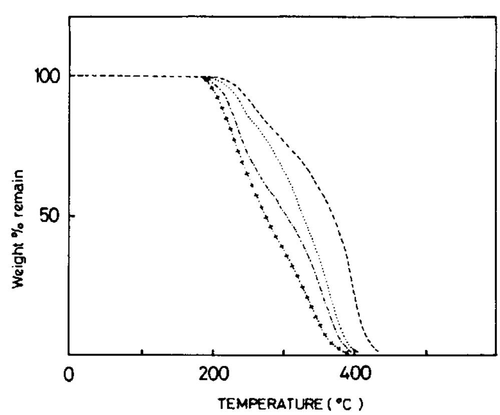

Fig. 2. Thermogram of poly(methyl methacrylate) (P-MMA). Influence of heating rate (°C/min): (+·+) 2; (-·-) 5; (· · ·) 10; (- - -) 30. E_a calcd: 25.57 ± 5.05 kcal/mol.

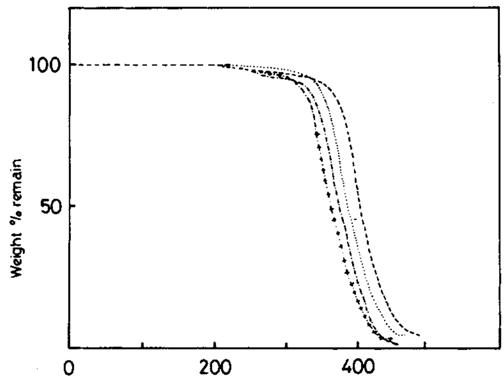

Fig. 3. Thermogram of grafted natural rubber (NR–P-MMA, 21%). Influence of heating rate (°C/min): (+·+) 2; (–·–) 5; (· · ·) 10; (- - -) 30. E_a calcd: 56.14 ± 6.02 kcal/mol.

field latex (41% total solid) was 5 cP.[9] The total solid markedly influences the viscosity. However, the total solid content is not the only factor which influences the viscosity. Although the P-MMA content is relatively low, if the irradiation

TABLE III
Grafting of MMA Monomer on Natural Rubber Latex: Influence of Irradiation Dose on the Viscosity, pH, P-MMA Content, and Toluene and Acetone Extracts of the Vulcanizates

Irradiation dose (krad)	P-MMA content (phr)	pH	Viscosity (cP)	Extracted by toluene (%)	Extracted by acetone (%)
		I. MMA addition: 10.7 phr			
0	0	10.13	13.51	5.135	3.93
25	0.33	10.15	14.23	5.23	3.89
50	1.38	10.15	18.71	5.38	4.01
75	2.71	10.17	39.26	5.31	4.45
100	3.89	10.17	49.91	5.50	4.01
200	6.72	10.18	77.63	6.19	3.97
300	7.73	10.18	a	6.22	3.94
		II. MMA addition: 21.4 phr			
0	0	10.10	18.26	5.01	4.05
25	1.0	10.12	19.09	5.70	4.40
50	4.85	10.13	26.11	5.37	3.99
75	7.65	10.16	53.97	5.40	3.99
100	9.88	10.17	100.30	5.60	4.06
200	14.51	10.17	253.27	6.26	4.00
300	16.23	10.21	a	8.54	4.26
		III. MMA addition: 32.0 phr			
0	0	10.02	19.21	5.07	4.14
25	5.30	10.02	20.73	5.23	5.23
50	13.24	10.03	31.04	5.45	4.08
75	14.90	10.04	60.09	5.63	4.09
100	18.01	10.05	69.03	6.83	3.82
200	22.30	10.04	195.05	7.61	3.93
300	24.79	10.07	a	6.98	4.22

Note: a = unmeasured.

TABLE IV
Grafting of MMA on Natural Rubber: Influence of P-MMA Content on the Tensile Strength and Elongation at Break of Pure Gum, Heated at 100°C

P-MMA content	Tensile strength (kg/cm^2)			Elongation at break (%)		
	Heating time (min)			Heating time (min)		
(phr)	30	45	60	30	45	60
0.00	279.40	263.70	235.73	760	764	714
0.12	312.79	312.33	286.56	828	838	—
0.94	295.73	301.33	301.85	819	828	—
1.89	310.02	294.03	301.51	821	823	—
2.33	261.30	285.02	291.52	703	737	740
3.51	305.58	310.95	279.39	774	767	719
4.82	268.84	275.67	248.70	—	—	—
6.14	282.91	280.42	263.98	771	790	—
8.12	293.99	268.68	244.38	738	704	681
10.34	298.49	257.13	269.62	760	738	—
14.61	262.21	280.71	253.63	719	737	686
14.83	252.36	234.93	268.86	—	—	—
17.68	248.41	251.23	236.24	—	—	—
21.49	280.06	261.77	251.46	671	657	648
26.00	—	266.69	—	—	671	—

Note: pure gum composition: rubber 100; sulfur 2; ZDC 2; dispersol, pepsin 0.2; ZnO 2.

dose is high, the viscosity is very high and not measureable by the available equipment (Table III). The film prepared from NR–MMA latex was good, in cases where the degree of grafting is lower than 25%. However, the vulcanized film had some cracks, in which the degree of crack depends on the P-MMA content or the degree of grafting. These experimental results showed that, at high degree of grafting or P-MMA content, the adhesive strength between the particles are poor.

TABLE V
Grafting of MMA on Natural Rubber: Influence of P-MMA Content on the Hardness of Pure Gum and the Swelling Ratio

P-MMA content	Hardness (Shore)			Swelling ratio in benzene		
	Heating time (min)			Heating time (min)		
(phr)	30	45	60	30	45	60
0.00	48.3	49	49	260	256	246
0.12	46.5	47.5	47	260	260	237
0.94	46.5	48	47.5	284	260	260
1.89	47.5	47.5	47.5	310	260	284
2.33	55	55	54	237	284	237
3.51	53	53	58	284	260	260
4.82	56	55	57	284	309	260
6.14	48	49	49.5	237	237	284
8.12	57	55	59	280	284	335
10.34	58	59	60	284	310	284
14.61	60	60	60	336	336	284
17.68	65	62	65	237	284	335
21.49	54	55	56	310	284	284

Note: composition of pure gum: rubber 100; sulfur 2; ZnO 2; ZDC 2; pepsin 0.2; temperature 100°C.

Extraction by Toluene and Acetone Solvent. The amount of extracted matter in acetone or toluene solvent from the vulcanized radiation grafted natural rubber (NR–MMA) prepared using radiation grafting does not differ much compared to the ungrafted one (Table III). A small increase in the amount of the extracted matter has been detected with the increase in the P-MMA content or degree of grafting. P-MMA is soluble either in toluene or acetone solvent; hence, the toluene and acetone extract contains either P-MMA and any non-rubber chemicals such as fat, accelerator, dispersol, emulsifier, etc. If it can be assumed that the untreated vulcanized rubber does not contain P-MMA, then the difference between the amount of the extracted matter in acetone or toluene solvents from the grafted NR and the ungrafted one is the soluble P-MMA. The remaining unsoluble P-MMA can be regarded as the grafted MMA on NR, which is insoluble either in toluene or acetone solvents. Hence, the ungrafted P-MMA is relatively very low, and this value increases with an increase in P-MMA content. P-MMA in the NR is largely grafted on NR.

Physical Properties. Tables IV and V show the physical properties of vulcanized rubber, either grafted or ungrafted. The influence of P-MMA content on the tensile strength and the elongation at break was not clear. A small increase in hardness with an increase in P-MMA content was detected. The influence of P-MMA content on the swelling ratio of the vulcanized grafted rubber also was not clear. The physical properties of the grafted rubber pure gum prepared by direct casting from the latex does not differ significantly compared to the ungrafted one. These experimental results are in agreement with the results of several studies dealing with grafting of NR using conventional method.[1]

CONCLUSION

Radiation can be used for the preparation of grafted natural rubber. In the case of radiation grafting of MMA monomer on natural rubber latex, an irradiation dose of 300 krad was needed to obtain 75% conversion.

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