STUDY ON GRAFTING OF MONOMER ONTO NATURAL RUBBER LATEX BY RADIATION TECHNIQUE

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ABSTRACT: Radiation vulcanization of natural rubber latex has been extensively developed through programmers assisted by the IAEA and UNDP under RCA in Asia and Pacific Region. R & D has been done in most of the Member States with technical assistance from Japan's Takasaki Radiation Chemistry Establishment.

Radiation vulcanized natural rubber latex (RVNRL) has many advantages over the conventional sulfur vulcanized latex, such as absence of nitrosamines and low cytotoxicity. Radiation crosslinking is a room temperature process, itself an important cost advantage, it is easily controlled and desired extend of crosslinking is easily achieved by controlling the dose (irradiation time). Disadvantages of RVNRL to be improved are poor physical properties of film such as low tensile strength and tear strength. The research groups of Japan, Thailand and Indonesia concentrated on the improvement of physical properties of RVNRL using radiation grafted PMMA as additive [2]. F. Sundardi and W. Sofiarti have reported that tensile strength and hardness increased by radiation grafting of styrene onto NR [5]. Ono et al have reported the grafting of MMA onto NR by gamma irradiation at a dose of 5 kGy for producing thermoplastic elastomers [4].

The objective of this project is to report the results of studies of radiation graft-copolymerization of methyl methacrylate (MMA) or styrene (St) onto natural rubber latex in order to improve their physico-mechanical properties and evaluation of grafted material using Small-Angle Neutron Scattering through FNCA Project. The grafting degree of MMA and St onto NR increased with the increase of irradiation dose and monomer concentration. The alteration of grafted products structure was determined by IR method. Tensile strength, Shore A hardness, 100% modulus of grafted products increased with the increase of monomer concentration and irradiation dose while elongation at break decreased. The grafted products were characterized by Transmission Electron Microscopy (TEM), Small-Angle Neutron Scattering (SANS) and Small Angle X-ray Scattering (SAXS).

I. THE CONTENT OF PROJECT

- Effects of monomer concentration and irradiation dose on grafting process.
- Evaluation of the mechanical property of grafted materials.
- Evaluation of the characteristics of structure of grafted materials by Transmission Electron Microscopy (TEM), Small Angle Neutron Scattering (SANS) and Small Angle X rays Scattering (SAXS).

II. OBTAINED RESULTS

II.1. Materials, Chemicals and Method

Natural rubber latex was received from Binh long Rubber Company. The total solid content (TSC) of the above-mentioned latex was about of 60%. Methylmethacrylate (MMA), Styrene (St) and others chemicals were analytical grade and were used without further purification.

The NR-g-PMMA and NR-g-PSt were carried out by mixing of centrifuged latex with emulsion of MMA at the concentrations of 25 phr, 50 phr and 75 phr (corresponding to MG25, MG50 and MG75 for MMA and SG25, SG50 and SG75 for St). The emulsion was prepared by mixing of MMA and NH_4OH 1% and adding 1% weight of laurylsulfate then stirring for 20 min. Radiation grafting copolymerization of PMMA and PSt onto natural rubber latex were carried out on gamma Co-60 source at 10 kGy for NR-g-PMMA and 50 kGy for NR-g-PSt .

The film samples of NR-g-PMMA and NR-g-PSt were prepared by casting method. After drying at room temperature until transparent, films were leached with water over night at room condition, and finally heating at 60°C for 1 hr. The films were extracted with aceton for NR-g-PMMA and with toluene for NR-g-PSt to remove homopolymers. The films of NR-g-PMMA and NR-g-PSt were cut into dumbbell shape pieces to measure mechanical properties. The grafted product characteristics such as Transmission Electron Microscopy (TEM), Small Angle Neutron Scattering (SANS) and Small Angle X rays Scattering (SAXS) were measured at Kyoto University through FNCA project.

II.2. Results

Degree of grafting: The grafting degree of MMA onto NRL increased with the increase of irradiation dose and monomer concentration. The grafting degree of MG25, MG50 and MG75 were obtained of 60%, 72% and 80% respectively, at irradiation dose of 6 kGy. And the grafting degree of SG25, SG50 and SG75 were 46%, 51% and 75% respectively, at 50 kGy.

Measurement of infrared spectrum: The alteration of grafted products structure was determined by IR method. The obtained results shown that the specific peaks for MMA and St was found to be 1731 cm^{-1} and 698,2 cm^{-1}, respectively.

Measurement of mechanical properties: The mechanical properties of grafted copoolymers were measured by TOYOSEIKI V10-C tester (ASTM D 638). The results were presented in Table 1 and 2.

Table 1: Mechanical properties of NR-g-PMMA

Dose (kGy)	**Tensile strength** (kg/cm^2)	**Elongation** (%)	**100% Modulus** (kg/cm^2)	**Shore A Hardness**
	I.MG25			
0	2.2	1278	0.437	
2	2.97	1045	0.442	
4	5.4	1007	0.356	
6	5.67	1023	0.541	
8	6.22	1002	0.571	
10	6.75	1003	0.566	
	II. MG50			
0	2.2	1278	0.437	35
2	4.62	863	0.54	45
4	7.67	803	0.779	55

6	9.78	812	0.878	57
8	11.78	827	0.906	57
10	10.98	816	0.906	58
	III. MG75			
0	2.2	1278	0.437	
2	7.9	806	0.774	
4	9.84	680	1.26	
6	11.56	667	1.444	
8	13.22	683	1.538	
10	13.21	662	1.559	

Table 2: Mechanical properties of NR-g-PSt

Dose (kGy)	**Tensile strength** (kg/cm^2)	**Elongation** (%)	**100% Modulus** (kg/cm^2)
	I. SG25		
0	2.2	1278	0.437
10	3.6	1171	0.502
20	4.43	1009	0.554
30	5.64	946	0.62
40	7.02	812	0.595
50	7.86	823	0.64
	II. SG50		
0	2.2	1278	0.437
10	6.81	998	0.779
20	9.34	850	0.9
30	11.1	798	1.064
40	12.2	678	1.162
50	14.24	668	1.157
	III. SG75		
0	2.2	1278	0.437
10	9,74	778	0.971
20	11.45	667	1.524
30	13.55	679	1.508
40	13.45	642	1.606
50	13.95	543	1.696

The alteration of phase structure of grafted copolymers: Characterization of grafted copolymers has been evaluated by Transmission Electron Microscopy (TEM), Small Angle Neutron Scattering (SANS) and Small Angle X rays Scattering (SAXS).

The results determined of grafted products shown that PMMA forms microdomains of the order of 20-50 nm in the matrix of NR, the average distance between PMMA microdomains is ca. 130 nm and the interfacial thickness between PMMA and NR phase is ca. 2 nm comparable to the value reported for PS-block-PI diblock copolymer. The dependence on gamma-ray dose was not observed by SAXS for the microdomain structure of grafted product.

Japanese expert concluded that NR thermoplastic elastomer were formed in excellent by radiation grafting copolymerization.

II.3. Conclusion

- The optimal doses for grafting of MMA and St onto natural rubber latex were found to be 6 and 50 kGy, respectively.
- The NR-g-PMMA and NR-g-PSt were determined by means of infrared spectrum and the function groups of MMA and St were characterized at 1731 cm^{-1} and 698.2 cm^{-1} respectively.
- The physico-mechanical properties of grafted products such as tensile strength, Shore A hardness and modulus increase in the increase of irradiation dose and concentration of monomer while elongation at break of grafted materials was decreased.
- NR thermoplastic elastomer was formed in excellent by radiation grafting copolymerization.

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