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ABSTRACT

RADIATION GRAFT COPOLYMERIZATION OF N-BUTYL ACRYLATE ON NATURAL RUBBER LATEX. A method of radiation graft-copolymerization of N-butyl acrylate (NBA) monomer on natural rubber (NR) latex has been studied. The rate of conversion increases with an increase in NBA in latex. An irradiation dose of about 12 kGy in needed to obtain a 90% conversion using 40 phr of NBA monomer in latex. Tensile strength, tear strength and elongation at break of grafted NR are found to decrease with an increase in degree of grafting. The physical strength of a vulcanizate from a mixture of NR and poly-NBA was found to be better than that of NBA grafted vulcanizates. Graft-copolymerization reaction takes place only in the outer layer of NR particles. The secondary bond between poly-NBA molecules are weaker than those between NR molecules , and hence the existence of poly-NBA layer in NR particles will decrease its physical strength.

ABSTRAK

KOPOLIMERISASI TEMPEL RADIASI N-BUTIL AKRILAT PADA LATEKS KARET ALAM. Telah dipelajari metode kopolimerisasi tempel monomer N-butil akrilat (NBA) pada lateks karet alam. Kecepatan konversi naik dengan naiknya kadar NBA pada lateks karet alam. Dosis radiasi sebesar 12 kGy diperlukan untuk mencapai konversi sebesar 90% dengan menggunakan monomer NBA sebesar 40 psk. Kekuatan tarik, ketahanan sobek dan perpanjangan putus vulkanisat karet kopolimer tempel ternyata turun dengan naiknya persen penempelan. Sifat vulkanisat campuran karet alam dengan poli-NBA ternyata lebih baik daripada sifat vulkanisat karet alam kopolimer tempel NBA. Reaksi kopolimerisasi tempel mungkin hanya terjadi di bagian luar partikel karet alam dalam lateks, sehingga karet kopolimer tempel dan poli-NBA hanya terbentuk di bagian luar partikel karet saja. Ikatan sekunder antar molekul poli-NBA lebih lemah daripada ikatan sekunder antar molekul karet alam, sehingga adanya lapisan luar poli-NBA dan karet kopolimer tempel pada partikel karet akan sangat menurunkan kekuatan fisiknya.

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INTRODUCTION

Radiation is found to be one of the useful tool for grafting of monomers on natural rubber (NR) latex. Research activities on radiation grafting of MMA, styrene, acrylonitrile and methyl acrylate monomers on NR latex have been carried out by a number of investigators. The main purpose of grafting of monomers on NR is to improve the physical properties of NR (1 - 6). An increase in hardness, tensile strength and modulus have been found.

The main purpose for radiation graft copolymerization of NBA monomer on NR latex is to get an oil resistant rubber. This paper presents the experimental results on the method of grafting NBA monomer on NR latex. The physical properties of grafted NR vulcanizates are also presented.

Radiation graft copolymerization of NBA monomer on NR latex can be regarded as a seeded radiation emulsion polymerization of NBA monomer, in which the NR particles act as the seed particles. The mechanism of seeded emulsion polymerization has been presented by a number of investigators such as HAWKETT _et al_. (7, 8). According to this theory, in seeded emulsion polymerization, there is no particle formation stage. The polymerization takes place inside the polymer particles, in this case NR particles, directly to the second or third stage of emulsion polymerization. Constant rate of conversion is found in the second stage of emulsion polymerization, but in the third stage the rate of conversion decreases with time. In cases where the monomer is limitedly soluble in NR, the graft copolymerization takes place only in the outer side of NR particles. In radiation grafting of NBA on NR latex, true emulsion polymerization also takes place through the formation of a new particle from the emulsifier micelles.

EXPERIMENTAL

Concentrated NR latex was obtained from Pasir Waringan Estate, West Java, Indonesia. The dry rubber content of the concentrated latex was about 60% by weight, and the viscosity was about 50 cP. N-butyl acrylate (NBA) monomer was purified by distillation under reduced pressure. Other chemicals such as oleic acid, ZnO, ZDC and sulphur were of technical grade and used without further purification.

Irradiation was carried out using a Panoramic Co-60 irradiator, 55 kCi activity. An irradiation dose rate of about 2 kGy per hour was selected for irradiation. Fricke dosimeter was used to calibrate the irradiation dose rate. A Toyo Seiki Test Mixing Machine was used for mixing the dry rubber with chemicals. An Instron Testing Machine, model 1122, was used to determine the physical properties of the vulcanizates. A given amount of NBA emulsion was added to a concentrated NR latex of about 60% dry rubber content. The NBA emulsion was prepared by stirring a mixture of 70 wt part of NH_3 solution in water (1.5 %), 30 wt part of NBA monomer, and 0.5 wt part of oleic acid. The mixture was stirred slowly by an electric stirrer, then irradiation. Irradiation dose were 3, 6, 9, and 12 kGy. The conversion of NBA monomer to polymer was determined gravimetrically just after irradiation. The NBA monomer which was converted to polymer was partly grafted on NR, and the rest was a hompolymer which may be entangled in NR mattrix. What is meant by grafted NR is actually an apparent grafted

NR which consists of true grafted NR and entangled poly-NBA in NR mattrix.

The grafted NR latex was then poured on a glass plate and dried. The dried film film was mixed with a given amount of sulphur vulca - nizing chemicals such as ZnO, ZDC and sulphur, in a Test Mixing Roll Machine. The mixture was cured for 60 minutes at 100°C, using a laboratory Test Press. The physical properties of the vulcanizates , i.e. tensile strength, elongation at break, modulus etc. were determined according to ASTM.

RESULTS AND DISCUSSION

Figure 1 shows a plots of conversion vs irradiation dose, for radiation graft copolymerization of NBA on NR latex. The rate of conversion increases with an increase in the monomer content in latex. By increasing NBA monomer in latex, there is a higher possibility of the monomer to form a new polymer particles , with the results in increasing the rate of conversion. Experimental results showed that radiation emulsion polymerization of NBA monomer can proceed fast. An irradiation dose of less than 0.6 kGy is enough to obtain a conversion of about 90% (9). It is seen that the rate of conversion is not constant as is expected from the seeded emulsion polymerization theory developed by HAWKETT et al.(7). So it appears that this grafting reaction is not purely a seeded emulsion copolymerization, but may be a mixture of a pure NBA emulsion polymerization and a seeded emulsion polymerization.

Table 1 shows the influence of poly-NBA content on the physical properties of the vulcanizate of mixture of NR and poly-NBA. A small amount of poly-NBA, i.e. up to 25 phr, increase the tensile strength of the vulcanizates, but a larger amount will decrease it. So far the amount of poly-NBA did not much influence the tear strength , elongation at break and hardness of the vulcanizates. In this case the existance of poly-NBA acts as a reinforcing filler.

Tables 2 and 3 show the physical properties of grafted NR vulcanizates. It appears that tensile strength, tear strength and elongation at break decreases with an increase in the percentage of grafting. A very low tensile strength and elongation at break were found when the percentage of grafting was around 30%. These experimental results can be explained by the assumption that the graft copolymerization takes place only on the outer layer of NR particles, due to the limited solubility of NBA monomer in NR. Hence every NR particles will be covered by poly-NBA or grafted NR layer which has a poor binding strength. This layer mostly consists of a saturated polymer in which the physical strength can not be improved by vulcanization. A small increase in hardness was found with an increase in the percentage of grafting. In this case grafted NR acts as a filler.

Table 4 shows the swelling ratio of grafted NR vulcanizates. It is seen that the swelling ratio decreases with an increase in the percentage of grafting. It means that grafted NR vulcanizates are more solvent resistant than NR vulcanizates. The swelling ratio for vulcanizates of a mixture of NR and poly-NBA can be seen in Table 5.This Table shows that poly-NBA content does not much influence the swelling ratio. It is clear that poly-NBA in NR can not improve its solvent resistance.

Table 6 shows the influence of grafting on the amount of materials extracted by benzene. It is seen that the amount of materials extracted by benzene is higher from NR vulcanizates than from grafted NR vulcanizates. The grafted NR layer in NR particles may act as a protector layer which will retard the diffusion of a solvent into NR particles. For information, poly-NBA is insoluble in benzene.

CONCLUSION

Radiation graft copolymerization of NBA monomer on NR latex is not a good method to improve the physical properties of NR. Although the solvent resistance of grafted NR vulcanizates was better than that of the ungrafted one, the tensile strength, tear strength and elongation at break of grafted NR vulcanizates were found to be very poor.

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Table 1. Physical properties of sulphur vulcanizates of a mixture of poly-NBA and natural rubber (NR).

poly-NBA content, phr	Tensile strength, kg/cm^2	Tear strength, kg/cm^2	Elongation at break , %	Permanent set , %	Hardness, Shore
0	154.6	12.0	633	3.33	45
5	163.2	12.8	630	6.66	46
10	208.6	10.0	683	3.33	45
15	197.3	8.2	683	5.83	45
20	169.3	10.7	680	3.33	45
25	197.0	7.3	697	5.83	43
30	132.7	12.5	627	5.55	43
35	152.8	12.0	671	6.66	43
40	77.5	10.7	530	8.33	45

Note :

Compound : sulphur 2, ZnO 2 ,ZDC 2, and NR 100

Table 2. Physical properties of sulphur vulcanizates of NBA-NR copolymer.

Dose, kGy	NBA, phr	p-NBA, phr	Tensile strength, kg/cm^2	Tear strength, kg/cm^2	E B, %	Hardness, Shore	P S, %
0	10	0	224.2	9.2	659	47.0	1.67
3	10	1.59	210.4	10.7	607	50.0	1.67
6	10	3.50	65.6	9.7	419	54.0	1.67
9	10	4.86	24.6	7.9	226	55.5	1.67
12	10	5.76	44.8	6.7	273	55.5	1.67
0	20	0	144.1	12.2	517	50.0	1.67
3	20	5.45	24.9	7.6	231	52.3	3.30
6	20	10.7	27.3	4.0	247	55.0	-
9	20	13.5	15.8	1.8	144	55.3	-
12	20	15.1	12.0	1.5	105	56.7	-
0	30	0	171.5	9.8	678	48.0	-
3	30	11.5	22.5	6.4	228	50.5	-
6	30	20.1	13.7	1.9	102	53.7	-
9	30	23.1	10.3	1.1	74	54.0	-
12	30	25.5	8.5	0.9	50	55.5	-
0	40	0	212.1	8.1	685	48.5	-
3	40	16.9	24.1	5.2	238	50.0	-
6	40	28.5	12.1	1.2	96	54.3	-
9	40	32.5	10.9	0.9	51	55.0	-
12	40	34.7	7.9	0.8	21	55.0	-

Notes: EB = elongation at break,

PS = permanent set

Compound : sulphur 2 , ZnO 2, ZDC 2, and NBA-NR 100

Table 3. Physical properties of sulphur vulcanizates of NBA-NR copolymer.

Dose, kGy	NBA, phr	p-NBA phr	Tensile strength, kg/cm^2	Tear strength, kg/cm^2	E B, %	Hardness, Shore	Permanent set, %
0	10	0	153.4	12.1	820	40.3	3.33
3	10	1.59	132.9	12.3	709	43.7	3.33
6	10	3.50	191.6	13.8	672	47.0	3.33
9	10	4.86	159.1	10.6	670	47.7	3.33
12	10	5.76	150.8	9.2	633	48.3	3.33
0	20	0	148.0	12.2	765	41.0	1.67
3	20	5.45	127.9	12.0	686	43.5	0.00
6	20	10.70	79.5	5.6	488	47.5	3.33
9	20	13.50	27.8	3.8	321	48.0	-
12	20	15.1	14.9	3.9	181	49.0	-
0	30	0	173.4	13.4	852	40.7	-
3	30	11.5	129.6	7.0	674	44.3	-
6	30	20.1	20.0	3.0	265	46.3	-
9	30	23.1	11.8	1.4	200	48.0	-
12	30	25.5	8.8	1.0	93	49.3	-
0	40	0	174.1	11.9	870	39.5	-
3	40	16.9	79.8	6.1	556	43.3	-
6	40	28.5	11.9	1.5	133	46.3	-
9	40	32.5	8.4	0.7	65	48.3	-
12	40	34.7	7.6	0.6	52	49.7	-

Note:

Compound composition : sulphur 1, ZnO 1, ZDC 1 and NBA-NR 100.

Table 4. Swelling ratio of NBA-NR vulcanizates in benzene.

Dose, kGy	NBA, phr	p-NBA, phr	Swelling ratio, % (volume)	
			I	II
0	10	0	467	336
3	10	0.35	406	324
6	10	3.40	392	312
9	10	4.77	357	322
12	10	5.62	371	319
0	20	0	467	336
3	20	5.75	399	262
6	20	11.03	377	310
9	20	13.67	350	316
12	20	15.33	356	284
0	30	0	467	370
3	30	10.89	428	336
6	30	20.38	378	323
9	30	23.60	391	303
12	30	25.72	349	297
0	40	0	483	363
3	40	16.17	436	349
6	40	27.90	398	323
9	40	32.00	349	291
12	40	34.34	323	284

Note:

Compound I: NBA-NR 100, sulphur 1, ZDC 1, and ZnO 1

II:NBA-NR 100, sulphur 2, ZDC 2, and ZnO 2

Table 5. Swelling ratio of a vulcanizate prepared from a mixture of poly-NBA and NR.

poly-NBA content, phr	swelling ratio, %	
	volume	weight
0	390	330
5	360	330
10	390	360
15	360	360
20	350	390
25	400	380
30	360	380
35	360	380

Note: compound, NR 100, sulphur 1, ZDC 1, and ZnO 1

Table 6. Fraction of grafted NR vulcanizates extracted by benzene.

Dose, kGy	poly-NBA, phr	weight fraction extracted	
		I	II
0	0	5.2	5.8
3	16.9	3.3	4.7
6	28.5	3.5	4.5
9	32.5	3.9	4.3
12	34.7	3.7	4.1

Note:

Compound I : NR grafted 100, sulphur 1, ZDC 1 and ZnO 1

Compound II: NR grafted 100, sulphur 2, ZDC 2 and ZnO 2

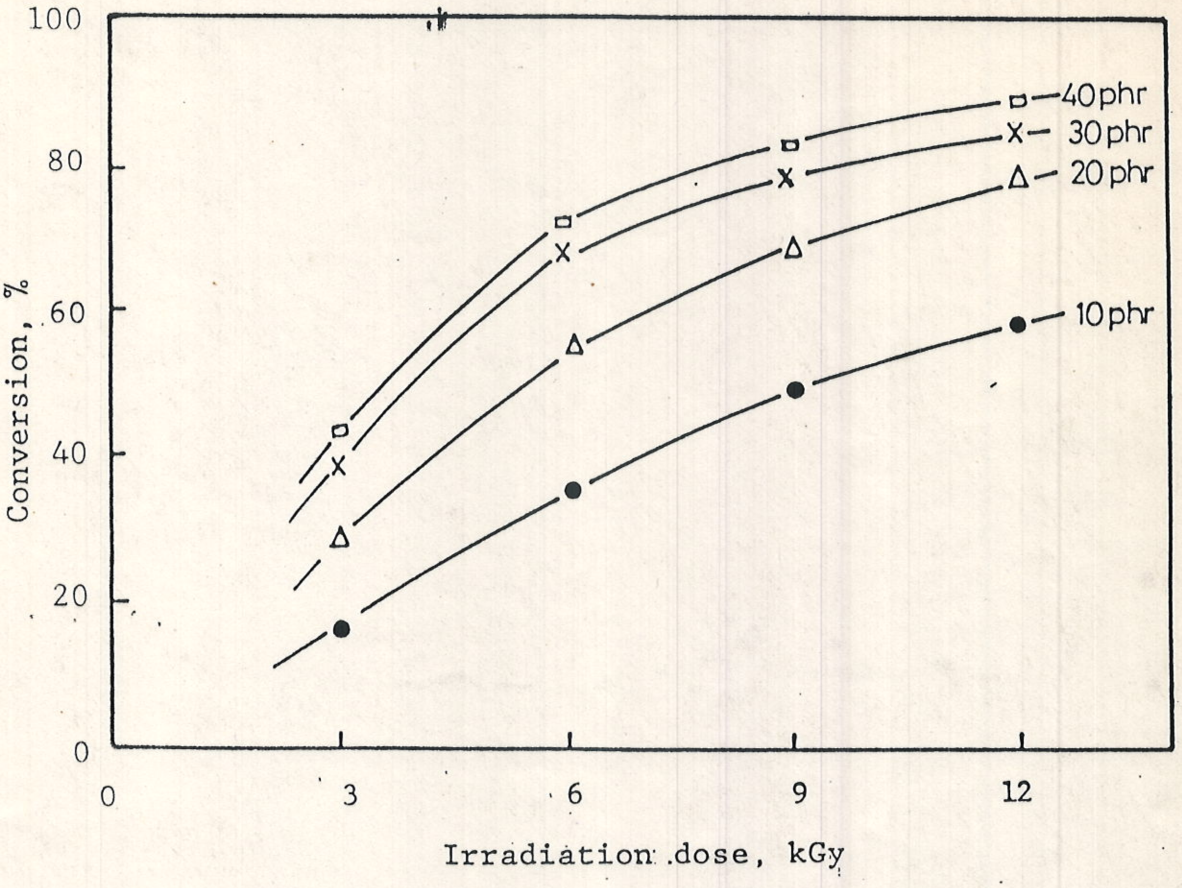

Figure 1. Radiation graft-copolymerization of N-butyl acrylate on Natural Rubber Latex.