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Effect of Radiation on Oil Extended Styrene-Butadiene Block Copolymer[1]

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ABSTRACT

Oil extended SBS containing various levels of photoinitiators, and crosslink agents were subjected to different UV and gamma irradiation dosages in nitrogen atmosphere; gel content, molecular weight(MW) and molecular weight distribution(MWD) excluding gel, tensile strength, modulus and elongation, T_g, and initial thermal degradation temperature were then measured. Crosslink density, expressed as gel content, was found proportional to radiation time but could not be correlated to physical strength changes; crosslink agent enhances gel formation but not the physical strength; MW excluding gel, dispersed wider after irradiation indicating both crosslink and scission occurred. Samples with 5 phr photoinitiator irradiated with 600 W UV lamp for 2 minutes at a distance of 30 cm, yield the best mechanical properties, while tensile strength at break and elongation increased 47.04% and 32.85%, respectively, and initial thermal degradation temperature and T_g increased 30.51℃ and 10.46℃, respectively. The addition of low molecular weight chemicals, such as extended oil, photoinitiator or crosslink agents, dilutes physical strength. Linear SBS requires less radiation dosage to reach the highest physical strength than the branched SBS. Tensile strength and elongation irradiated with gamma ray decreased with increased dosage, but $TS_{300\%}$ and T_g increased. Physical strength of SBS is dominated by the hard block, radiation do not carry it beyond samples without extend oil.

Key words: radiation vulcanization, UV radiation, and radiation crosslinking of SBS

Introduction

The effect of radiation vulcanization on the physical properties of SBR (styrene butadiene random copolymer) has attracted the attention of many researchers. E. Witt (1959) found that there was a transfer of radiation energy from butadiene to styrene units; thus crosslinking yield is decreased as styrene content increases. Youssef H. A. and Xu Tunshu (1993-1994) found that multifunctional monomers can improve mech- anical properties and tetramethylolmethane tetra- acrylate could effectively reduced the required radiation dose for vulcanization, and the mechanical properties, like tensile strength, tensile stress, tensile yield, and hardness of the radiation cured

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vulcanizate were higher than those of sulfur cured vulcanizate. They also showed that the effect of styrene content on the properties of electron-vulcanized SBS containing carbon block was conspicuous only at low irradiation doses.

Information on the vulcanization of SBS block copolymer is few. C. Wang (1997) found that SBS specimens crosslinked with 0.01 phr DCP enhanced tear strength at high temperatures. Yang Huai (1993) concluded that 1,2-butadiene has greater crosslinking efficiency. US Patent 4133731 (1979) described that when SBS or SIS added with 25 to 250 phr tackifying resin and 1 to 50 phr di-to tetrafunctional acrylate or metha- acrylate and then vulcanized by UV or electron beam, samples have excellent cohesive strength at high temperature along with excellent adhesion, shear strength and solvent resistance. Decker (1999,2000) published a series of investigation on UV cured SBS. The thickness of SBS used in these investigations was 20 μm. They found that the order of increasing efficiency of photoinitiator SBS UV curing: Bisazide< benzophenone< Irgacure 651< Irgacure 184< Lucirin TPO. An increase of the photoinitiator concentration can increase crosslink density and efficiency. Although the initial rate of gelation of low vinyl content of SBS was lower than high vinyl content of SBS, but the crosslink density of these samples was similar. This was attributed to increasing intramolecular polymerization between neighboring pendent double bonds resulting from increasing the effect of vinyl content of SBS on UV curing, without increasing intermolecular polymerization. The rate of vinyl polymerization was increasing with adding Nujol, a parafinic oil, in SBS. This was explained as increasing intermolecular polymerization resulting from increasing the molecular mobility of the SBS chains. Branched SBS of 1wt% TRIS (trimethylolpropane mercaptopropionate) required less time to become insoluble than linear SBS containing the same amount of TRIS. This was attributed to increasing crosslink density resulting from the branched structure of the elastomeric phase.

In view of Wang's and US patent 4,133,731's results, the purpose of this research was to investigate the physical properties of radiation vulcanized SBS.

Experimental

Materials

Styrene-butadiene block copolymer used in this study were TPE 4402, Kraton D 1101, and 1122, commercial grades from TSRC Co. and Shell Co., respectively. The properties of SBS is listed in table 1. The photoinitiator (Suncure 84, benzoyl-1-cyclohexanol) and crosslink agent, divinyl benzene were supplied by Sunko Chem. and Pharchutical Co. and TCI Co. LTD., respectively.

Preparation of samples and irradiation

Samples of 1 ㎜ thick were film casted from 20% SBS toluene solution at 45℃, and then die cut into dumbbell shaped samples(CNS No. 3). The compositions of samples were listed in Table 2. Samples irradiated with UV light were enclosed in quartz tube, flushed with nitrogen,

Table 1 the properties of SBS

	styrene (wt.%)	vinyl (wt.%)	extended oil (phr)	Gel fraction (wt.%)	Hardness	Mw $\times 10^3$	Mn $\times 10^3$	MWD
Karton D 1101	31.69	9.8	none	0	80	204.4	132.5	1.543
Karton D 1122	40	9.4	none	0	97	145	91	1.593
TPE 4402	40	11.5	34	0	76	105.8	96.6	1.095

Table 2 the composition of UV irradiared samples

Sample	Polymer	Photoinitiator （phr）	Crosslink agent （phr）	vulcanized method
N1	TPE 4402	0	0	UV
N2	TPE 4402	1	0	UV
N3	TPE 4402	3	0	UV
N4	TPE 4402	5	0	UV
N5	TPE 4402	8	0	UV
N6	TPE 4402	5	1.6	UV
N7	TPE 4402	5	3.2	UV
N8	TPE 4402	5	4.78	UV
N9	TPE 4402	5	6.38	UV
N10	TPE 4402	5	12.23	UV
N11	Kraton D 1101	0	6.38	gamma ray
N12	Kraton D 1122	0	6.38	gamma ray

sealed, and subjected to irradiation with a medium pressure 600 W, 7 ㎝ long mercury lamp placed 30 ㎝ away from the sample. The source of gamm ray in this studied is Cobalt-60 supplied by China Biotech Co. and the dosage were 48.3, 104.3, 152.3, 224.9, and 232.4 KGy, respectively.

Physical properties

Tensile strength, Elongation and modulus were determined using tensile machine (GT-7010A_2-PC, Gotech Co.) with crosshead speed of 300 ㎜/min. Thermal degradation temperature and glass transition temperature (T_g) were determined by Thermalgravimetric Analyzer (TGA, type, 951, Du Pont Co.) and Differential Scanning Calorimeter (DSC, type, 910, Du Pont Co.) heated at a rate of 20℃/min in nitrogen.

Gel fraction

A known amount of polymer was dissolved in toluene, and then the sample was filtered through a 0.2 μm media and the recovered solid was washed with fresh solvent, dried and weighted. The gel content was determined as follows:

Gel content = (solid weight / initial weight of sample)×100%……... （1）

Molecular weight and distribution (MWD)

Molecular weight and distribution of filtrates from gel fraction measurement were determined by Gel Permeation Chromato-graph (GPC, type, L 7100, Hitachi Co.). Sample containing 1.5 mg/ml solution was injected onto columns at a flow rate of 1 ml/min. Polystyrene was used as standard.

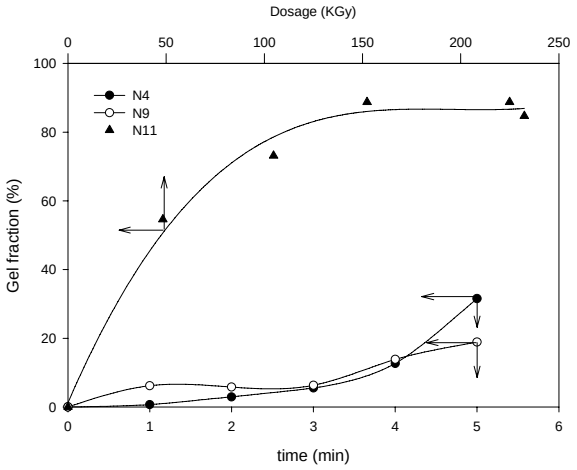

Figure 1 effect of irradiated time/dosage on gel fraction (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB, N11 Kraton D 1101 + 6.38 phr DVB)

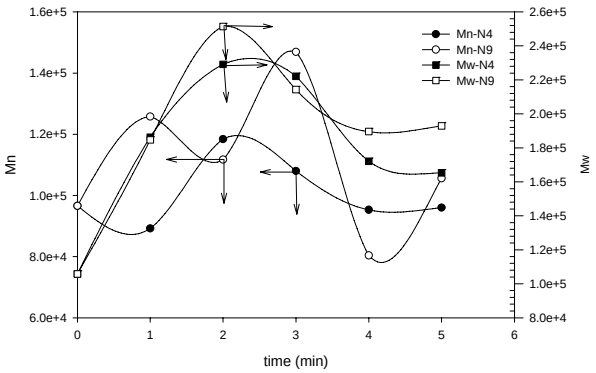

Figure 3 effect of radiation vulcanization on molecular weight (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB, N11 Kraton D 1101 + 6.38 phr DVB)

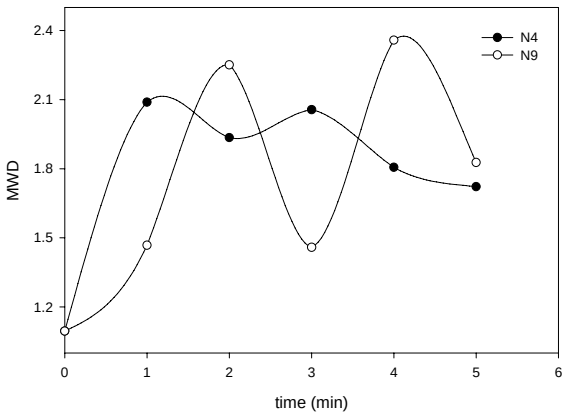

Figure 2 effect of radiation vulcanization on MWD (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

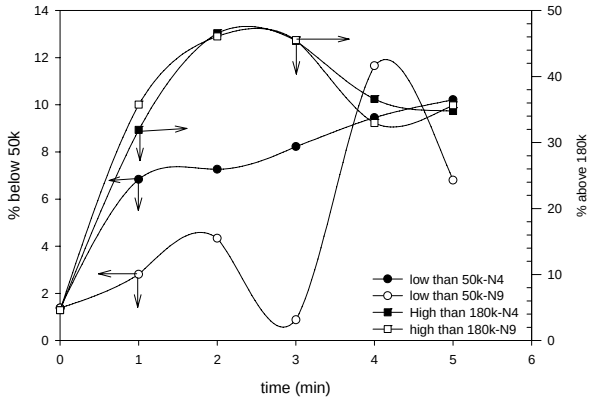

Figure 4 effect of radiation vulcanization on molecular weight fractions (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

Results and discussion

Effect of UV radiation on Gel content, MW and MWD

As shown in figure 1, gel fraction increases as irradiated time increases. It was observed that the gel generated in UV irradiation form a thin casing with fine apertures, but in gamma irradiation, gel was in cubic form. This can be attributed to the low penetrability of UV light, so , crosslinking only can occur on the surface of SBS. But gamma ray can penetrate SBS, so that crosslinking can occur at the inside of SBS. This also explains why the gel content was much higher in gamma radiation.

Figure 2 and 3 indicated that, after crosslinked gel were filtrated out, the MWD becomes broader and both Mn and Mw increased, indicated that the UV radiation caused at least two reactions, crosslink and scission, and the molecules caused by chain scission may also

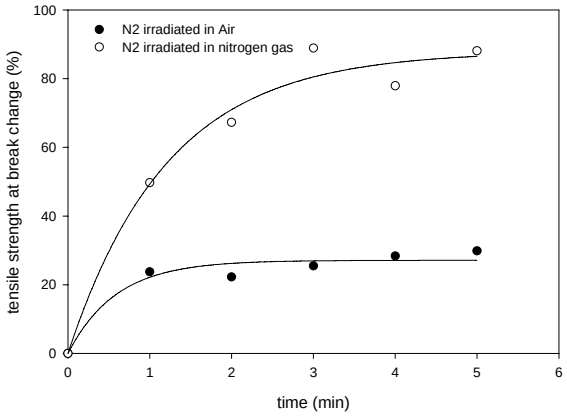

Figure 5 effect of radiation atmosphere on tensile strength (N2:TPE 4402 + 1 phr Suncure 84)

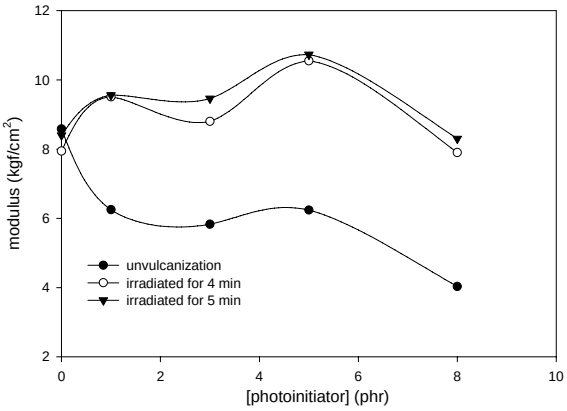

Figure 7 effect of photoinitiator concentration on modulus

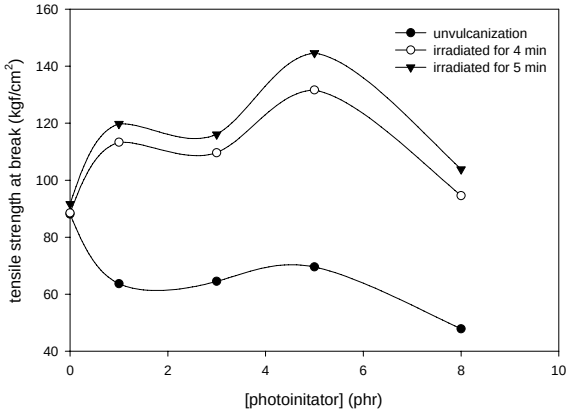

Figure 6 effect of photoinitiator concentration on tensile strength

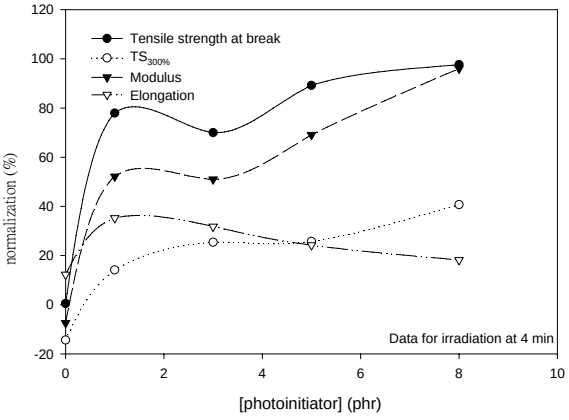

Figure 8 effect of effect of photoinitiator concentration on physical properties (normalization)

crosslink again in the presence of crosslink agent. As shown in figure 4, the fraction of molecular weight above 180,000 was similar for specimens contained DVB and without DVB, specimens containing DVB had fewer fraction of molecular weight below 50,000 than that without DVB, and the fraction of molecular weight below 50,000 of the specimens without DVB increased with increasing radiation time, but specimens containing DVB was not always increased with increasing radiation time. This can be assumed that DVB promoted crosslink.

Effect of radiation atmosphere

Figure 5 showed that SBS irradiated in nitrogen had better tensile strength than those irradiated in air, indicating that radiation oxidative degradation existed and the change in tensile strength peak at 5 min. irradiated time.

Effect of photoinitiator concentration

Figure 6 and 7 was the effect of photo- initiator concentration on tensile strength, and modulus of SBS.

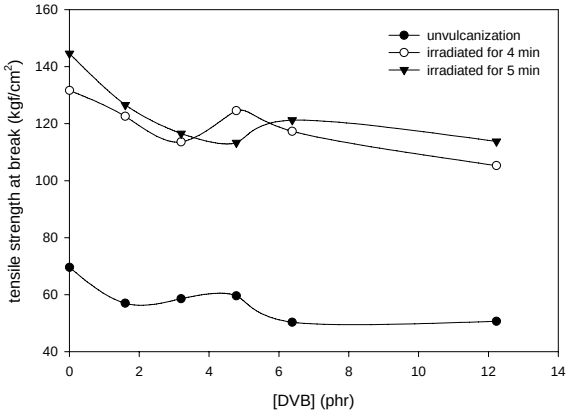

Figure 9 effect of DVB concentration on tensile strength

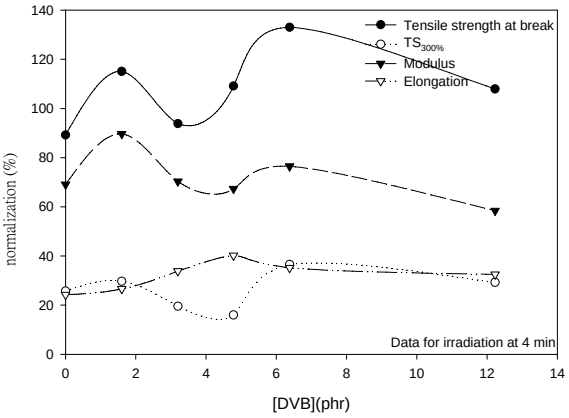

Figure 11 effect of effect of DVB concentration on physical properties (normalization)

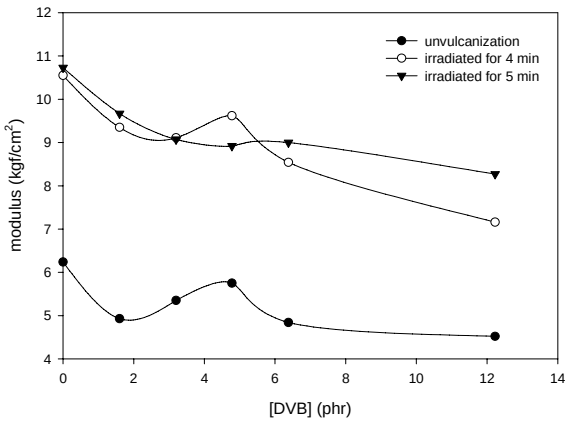

Figure 10 effect of DVB concentration on modulus

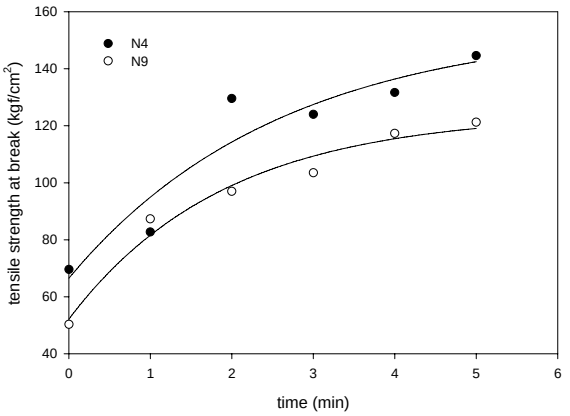

Figure 12 effect of irradiated time on tensile strength (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

As shown in the figure, addition of photoinitiator diluted physical strength, the difference in tensile strength and modulus before and after irradiation increased to the highest value at 5 phr photoinitiator. Further increase in photo- initiator concentration lowered tensile strength and modulus but the difference maintained as the effect of chain scission continued and dominated.

As shown in figure 8, without considering diluted effect, tensile strength, modulus and $TS_{300\%}$ increased, but elongation decreased with increased photoinitiator concentration. The increase in tensile strength, modulus and $TS_{300\%}$ can be attributed to accelerative crosslink density caused by the additional free radicals resulting from the increased photoinitiator concentration. The increased crosslink density also restricted molecule movement, which caused the decrease in elongation. Consequently, an increase in photoinitiator concentration will both accelerate

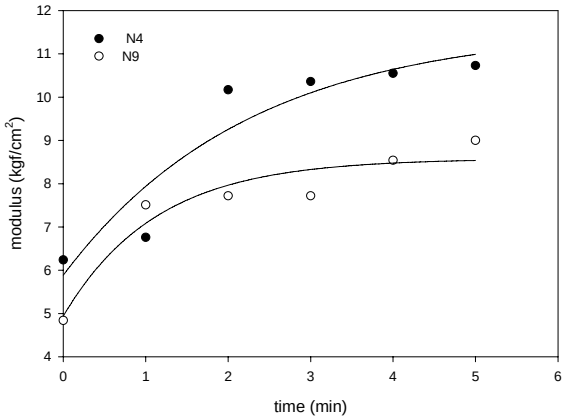

Figure 13 ffect of irradiated time on modulus (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

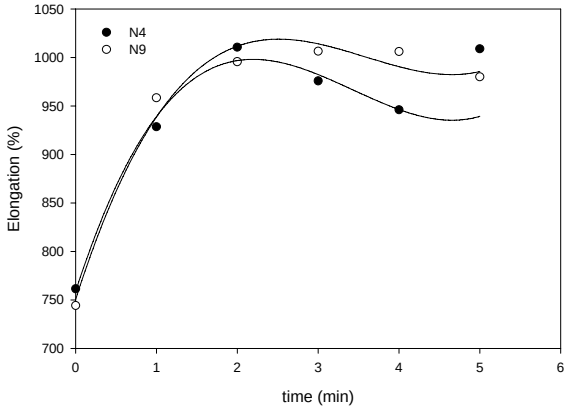

Figure15 effect of irradiated time on elongation (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

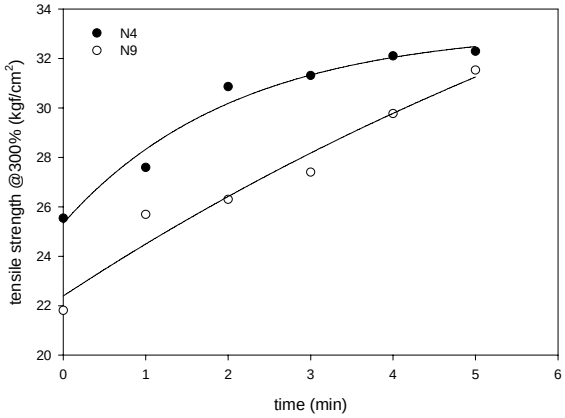

Figure14 effect of irradiated time on $TS_{300\%}$ (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

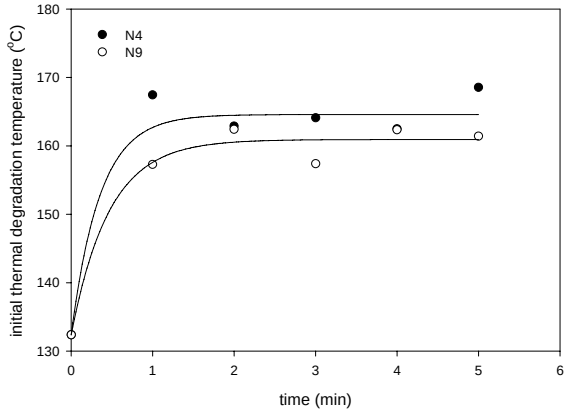

Figure16 effect of irradiated time on thermal degradation temperature (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

reaction and cause diluted effect. After considered all of these effects on photoinitiator concentration, the best concentration of photoinitiator was 5 phr.

Effect of DVB concentration

As shown in Figure 9, 10 and 11, the addition of the DVB did not enhance tensile strength and modulus, the diluted effect was dominating.

Effect of irradiated time on the physical properties, T_g and thermal degradation temperature

As shown in figure 12, 13 and 14 tensile strength, modulus and $TS_{300\%}$ increased as increasing irradiated time. The increased in modulus can be explained by following equations:

$$E = \frac{3\rho RT}{M_c} \quad \text{.....(2)}$$

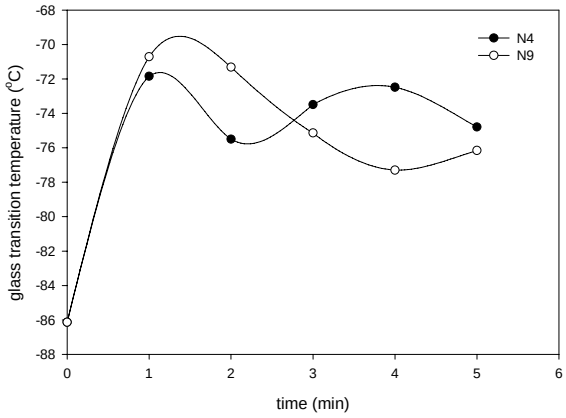

Figure 17 effect of irradiated time on glass transition temperature (N4:TPE 4402 + 5 phr SunCure 84, N9:TPE4402 + 5 phr Suncure 84 + 4.78 phr DVB)

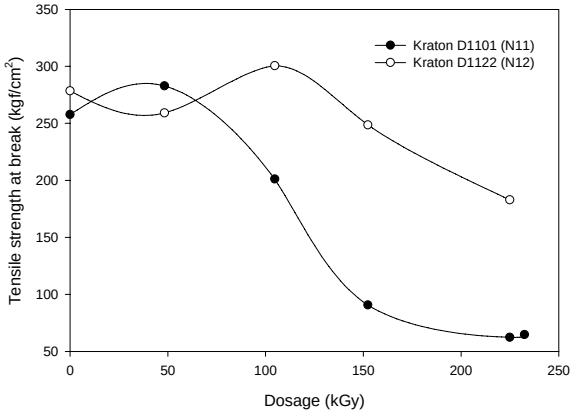

Figure 18 effect of structure of SBS on tensile strength (samples contained 6.38 phr DVB)

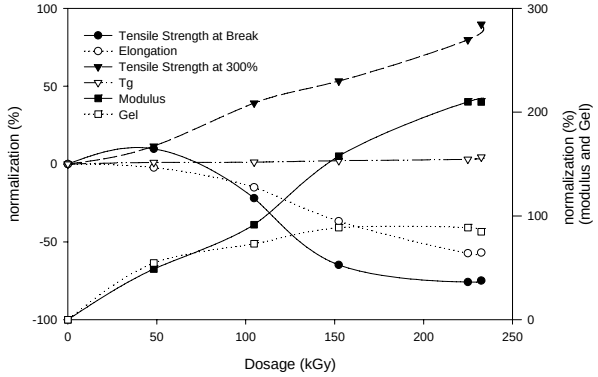

Figure 19 effect of radiation vulcanization on the properties of Kraton D 1101 (samples contained 6.38 phr DVB)

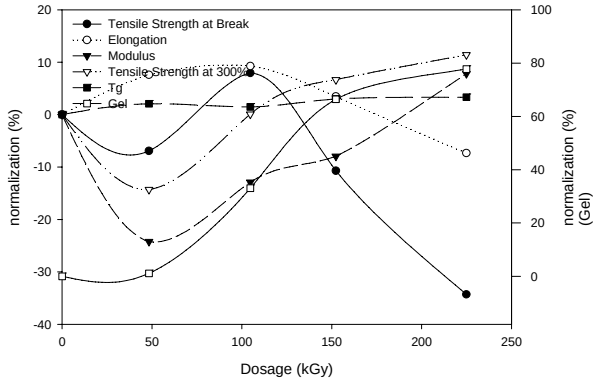

Figure 20 effect of radiation vulcanization on the properties of Kraton D 1122 (samples contained 6.38 phr DVB)

after radiation vulcanization,

$$M_c = \frac{0.48 \times 10^6}{G_x D} \quad \text{.....(3)}$$

where E is the modulus, ρ is the density, R is the gas constant, Mc is the number-average molecular weight of the network chains, Gx is the yield of crosslink, D is the dosage. From equation (3), with increased crosslink density, Mc shall decreased and modulus increased. The increase in tensile strength can also be attributed to the higher crosslink density. The elongation increased in the early period of irradiation, and then decreased with increasing irradiated time. The behavior of elongation can be explained by reasons:

1. In the early period of irradiation, the interaction of the polymer chains increased, so that the elongation of SBS will increase. But with increasing irradiated time, the rigidity if SBS increased, thus the elongation of SBS will decrease.

Table 3 effect of irradiated time on physicals properties of oil extended SBS (TPE 4402+10 phr SunCure 84)

time (min)	tensile strength (kgf/cm^2)	elongation (%)	modulus (kgf/cm^2)	$TS_{300\%}$ (kgf/cm^2)
0	38.42	732.41	3.52	18.80
1	53.29	844.84	4.99	24.72
3	57.70	844.28	5.41	26.00
5	66.75	961.95	5.80	26.78
10	61.02	752.76	6.93	30.31
20	2.17	267.39	—	—

In the early period of irradiated time, the reaction of irradiation is favor to crosslinking, but degradation dominated later.

The behavior of thermal degradation temperature and glass transition temperature was shown in figure 16 and 17. Thermal degradation temperature and glass transition temperature increased after radiation. The rise in T_g is caused by the restricted of chain movement resulting from crosslinking. The reason of thermal degradation temperature increase is that for a linear polymer, only one equivalent bond cause to break up of polymer chain, but for crosslinked polymer need two or more equivalent bond broken to cause the chain of polymer breaks down to volatile products.

After consider the effect of irradiation time and dilution of low molecular chemical, such as photoinitiator and crosskink agent, described above, samples with 5 phr photoinitiator irradiated with 600 W UV lamp for 2 minutes at a distance of 30 cm, yield the best mechanical properties. Tensile strength at break and elongation risen 47.04% and 32.85%, respectively, and initial thermal degradation temperature and T_g risen 30.51 ℃ and 10.46 ℃, respectively.

Effect of the structure of SBS on radiation vulcanized

As shown in table 3 the tensile strength, modulus and $TS_{300\%}$ of TPE 4402 improved in the early stage of irradiation. But for longer irradiated time, i.e. 20 min, the tensile strength and elongation of specimens decreased. So, the character can be use to design the optimum time of irradiation to reach the best physical properties. As shown in figure 18, linear and branched SBS reached the best physical properties at 50 and 100 KGy, respectively. So, the dosage required to achieve the best physical properties of linear SBS lower than branched SBS. Figure 19 and 20 show that modulus, $TS_{300\%}$, T_g and gel increased with increasing dosage. But elongation and tensile strength decreased after a certain value of dosage.

Conclusion

From the data of oil extended SBS with 1 to 8 phr photoinitiator vulcanized by UV radiation for 0 to 5 minutes, the average values of tensile strength at break and elongation risen 12.53% and 26.91%, respectively, and the average value of initial thermal degradation temperature and T_g risen 28.27℃ and 10.17℃, respectively. Samples with 5 phr photoinitiator and irradiated with 600 W UV lamp for 2 minutes at a distance of 30 cm, yield the best mechanical properties. Tensile strength at break and elongation risen 47.04% and 32.85%, respectively, and initial thermal degradation temperature and T_g risen 30.51 ℃ and 10.46 ℃, respectively. The addition of low molecular weight chemicals, such as photo- initiator and crosslink agents, has dilution effects on the physical strength. Crosslink agent enhances crosslink density, but did not improve strength. The dosage required to achieve

the best physical properties of linear SBS lower than branched SBS.

Crosslink density, expressed as gel content, was proportional to irradiation time, but could not be related to physical property changes. The average molecular weight excluding gel, increased and the distribution of molecular weight became broader, indicating that both chain scission and crosslinking occurred.

Although, radiation vulcanization can improve the physical properties of oil extended SBS, but the physical properties of SBS is dominated by the styrene block of SBS. Results from this work indicating that radiation vulcanized oil extended SBS is lower in strength than non-oil non-vulcanized SBS.

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