Variation with radiation dose of tensile strength and elongation at break of styrene–butadiene–styrene triblock copolymer

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The variation of tensile strength and elongation at break of styrene–butadiene–styrene triblock copolymer containing 34.1, 40.0 and 52.5% styrene have been studied with respect to their morphology and the extent of crosslinking produced by irradiation with ^{60}Co rays. We assume that the existence of microphase separation between polybutadiene (PB) and polystyrene domains and entanglements between PB segments result in the unusual variation of the two characteristics with radiation dose, which is different from that in common elastomers and blends.

(Keywords: triblock copolymer; radiation; tensile strength)

Introduction

There have been many reports about the mechanical properties of irradiated polybutadiene (PB), polystyrene (PS), PB/PS blends and butadiene–styrene copolymer. In all cases, the tensile strength and elongation at break increase at first with radiation dose increase, and then begin to decrease after passing through a maximum, although the extents of variation differ. Like PB/PS blends, and unlike butadiene–styrene copolymer, PB and PS blocks in styrene–butadiene–styrene (SBS) copolymer tend to form separated phases owing to thermodynamic incompatibility. However, only microphase separation morphology is possible because of the existence of chemical bonds linking the styrene and butadiene segments. In a sample containing a lower proportion of styrene, PB blocks exist as a continuous phase while PS domains disperse in the PB matrix. In a sample containing a medium proportion of styrene, the two domains tend to be continuous[1]. This kind of structure results in an unusual variation of mechanical properties of irradiated SBS copolymer with radiation dose, which is different from that found in common elastomers. In a previous paper[2], non-random radiation crosslinking of SBS triblock copolymer was discussed. In this paper, the variation of tensile strength and elongation at break of the samples with radiation dose, which has not been reported to date, is studied, and a possible explanation is given considering the structure of the samples.

Experimental

Samples. The characteristics of the block copolymers studied are listed in *Table 1*.

Irradiation. The samples were irradiated with ^{60}Co γ rays in vacuum at room temperature, with a dose rate of 7.8 kGy h^{-1}.

Characterization. Mechanical properties were measured by an Instron model 1122 Tensile Tester with a crosshead speed of 50 mm min^{-1} at room temperature. Glass transition temperatures were determined with a DDV-II-EA viscoelastometer at a frequency of 3.5 Hz in the temperature range -150 to 150°C.

Results and discussion

The mechanical properties of irradiated SBS copolymer obtained from tensile testing at room temperature are listed in *Table 2*. It is seen that, with radiation dose increase, both tensile strength and elongation at break of the samples decrease at the initial radiation stage, then increase when the dose increases further (middle radiation stage), and then decrease again at the late radiation stage.

Considering the structure of the SBS copolymer, we assume that the variation of the two characteristics at the initial radiation stage is due to microphase separation and entanglements. Holden *et al.*[3] demonstrated that not only is microphase separation present, but also entanglements between elastic butadiene chains. PS blocks play the role of physical crosslinking points. These entanglements are not knots, but interloopings which may slip without disengaging. Thus, a chain between entanglements, which is initially short in the direction of stress, is elongated by slippage of the terminal entanglements when being stretched, and the stress is also more evenly distributed in this way. So SBS copolymer has a high tensile strength and elongation at break. The reason why the two characteristics decrease with dose at the initial radiation stage, we assume, is that as soon as the crosslinking is produced after irradiation, the chains linked by crosslinking cannot slip relatively because the crosslinking points are no longer interloopings but are knots. They will tend to break because they cannot be elongated to the extent of the interloopings, and there is much load on them if they are stretched. Catastrophic failure may then result from the

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Table 1 Composition and microstructure of copolymers studied

Sample	PS content[a] (wt%)	Microstructure (%)[a]			$M_w \times 10^{-3}$[b]	$M_n \times 10^{-3}$[c]
		cis	*trans*	vinyl		
SBS-1	34.1	32.8	59.4	7.8	100	85.5
SBS-2	40.0	31.8	59.9	8.3	100	84.7
SBS-3	52.5	31.4	59.6	9.0	100	85.6

[a] From n.m.r. measurement
[b] Determined by light scattering
[c] Determined by membrane osmometry

Table 2 Tensile strength and elongation at break of irradiated samples at room temperature

Dose (kGy)	SBS-1		SBS-2		SBS-3	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0.0	22.77	1630	26.04	1381	30.61	1329
9.8	17.70	1470	24.64	1375	30.53	1325
19.8	27.49	1660	18.38	912	25.78	1223
38.3	29.10	1682	23.01	1294	13.40	863
59.4	29.70	1585	26.19	1277	17.42	972
106.6	17.33	1050	19.37	1075	18.38	1053
155.5	17.35	1026	18.42	926	20.56	1011
195.9	12.38	725	14.82	834	20.27	930
245.0	10.31	662	11.08	720	17.03	764
301.7	8.46	685	9.35	655	16.89	584
407.0	6.25	527	7.83	501	14.42	460

Table 3 Tensile strength and elongation at break of irradiated samples at 125°C

Dose (kGy)	SBS-1		SBS-2	
	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0.0	0.19	21	0.24	14
12.1	0.26	66	0.25	32
34.3	0.28	387	0.29	278
63.8	0.58	666	0.47	409
110.5	1.31	357	0.91	331
174.3	1.35	265	1.14	255
242.5	1.48	175	1.29	124

repeated transfer of stress in this way. So the tensile strength and the elongation at break decrease. To demonstrate this, we measured the two characteristics at 125°C above the glass transition temperature of styrene segments before and after irradiation. The results, listed in *Table 3*, show that the tensile strength of irradiated SBS is higher than that of the unirradiated sample and increases with dose. The elongation at break increases with dose at first, and then begins to decrease after a maximum. This agrees with the changed law of common elastomers affected by irradiation. This is because PS blocks become soft at high temperature and no longer behave as physical crosslinking points. The radiation-induced crosslinking plays the main role.

The reason why the two characteristics increase a little with dose increase at the middle radiation stage may be that more crosslinking is produced and they distribute relatively more uniformly. But then they decrease again when samples are irradiated further because a certain amount of crosslinking makes the sample brittle. *Table 2* also indicates that the two characteristics decrease more and more at the initial radiation stage (for example, the difference between the original value and the minimum tensile strength at the initial stage is 5.07, 7.66 and 17.21 MPa for SBS-1, SBS-2 and SBS-3, respectively), and increase less and less at the middle radiation stage with increasing content of styrene segments.

Considering the deformation of the PS microdomains in the stretching processes, perhaps we can give a reasonable explanation. Hashimoto *et al.*[4] reveal that when an SBS sample containing a continuous PS microdomain is stretched, the deformation processes of PS microdomains include the following: (1) the connection between PS microdomains parallel to the stretch direction is destroyed and the microdomains become lamellae perpendicular to the stretch direction; (2) further shearing, kink, disruption and orientation of the lamellar microdomains occur; (3) PS lamellae are completely disrupted and become small oval particles dispersed in the PB matrix.

We have measured the glass transition temperatures of the three samples and they are listed in *Table 4*. T_{g1} is attributed to butadiene segments and T_{g2} to styrene segments. We can see that T_{g1} decreases and T_{g2} increases with increase in content of styrene segments. The reason is that there is a better compatibility between the styrene and butadiene domains in the sample containing a lower proportion of styrene than in that containing a medium proportion of styrene, according to the domain boundary mixing and mixing-in-domain effects[5]; i.e. the PS

Table 4 The glass transition temperatures for the samples

	SBS-1	SBS-2	SBS-3
T_{g1}	−82.6	−83.4	−83.8
T_{g2}	98.7	102.9	104.8

Table 5 Tensile strength and elongation at break of irradiated pre-stretched samples of SBS-2 and SBS-3 at room temperature

	SBS-2		SBS-3	
Dose (kGy)	Tensile strength (MPa)	Elongation (%)	Tensile strength (MPa)	Elongation (%)
0.0	25.82	1390	28.31	1331
9.8	25.73	1324	28.36	1340
19.8	19.41	1197	24.45	1294
38.3	22.00	1315	18.61	1078
59.4	25.94	1302	21.79	1170
106.6	20.70	1194	22.40	1216
155.5	18.60	944	24.30	1180
195.9	15.16	890	20.83	901
245.0	12.80	803	18.36	779
301.7	9.94	681	16.77	591

microdomains in SBS-2 tend to be more continuous than those in SBS-1, as do the PS microdomains in SBS-3 compared to those in SBS-2. Therefore a greater deformation of styrene microdomains will be produced and a greater load will be concentrated on some butadiene chains in SBS-2 and SBS-3 than in SBS-1 and SBS-2, respectively. So the mechanical properties decrease more and increase less at initial and middle radiation stages, respectively.

We also measured the two mechanical properties at room temperature of samples that were stretched to five times the original length and then released, before being irradiated; the results are listed in *Table 5*. It can be seen that the properties of SBS-2 and SBS-3 decrease less at the initial radiation stage and increase more at the middle radiation stage than those of the corresponding unstretched samples. This proves that the above-mentioned hypothesis is reasonable.

Conclusions

The existence of entanglements between the elastic butadiene chains results in an overall decrease in both tensile strength and elongation at break with increase in radiation dose, although both characteristics increase to some extent when the samples are radiated at a certain dose. The ratio of styrene/butadiene and the morphology of the styrene blocks also affect the two mechanical properties.

All experiments were repeated and the patterns of results were almost the same, indicating that the results are very reliable. Explanations of the effects are somewhat speculative, and further study will be carried out.

References

1 Noshay, A. and McGrath, J. E. 'Block Copolymers, Overview and Critical Survey', New York, 1977, Ch. 4
2 Yang, H., Zhao, Z. and Chen, X. *Radiat. Phys. Chem.* 1993, **41** (3), 491
3 Holden, G., Bishop, E. T. and Legge, N. R. *J. Polym. Sci., Part C* 1969, **26**, 37
4 Hashimoto, T. *et al. Macromolecules* 1983, **16**, 648
5 Stuart, L. and Cooper, G. M. E. 'Multiphase Polymers', American Chemical Society, 1979, Ch. 14