Relaxation of Stress in Polypropylene and Ethylene–Propylene–Diene Elastomer Blend Vulcanizates at Moderate and High Extensions

ABHIK SENGUPTA, BIDYUT BARAN KONAR

Department of Polymer Science and Technology, Calcutta University, Calcutta-700009, India

Received 11 September 1997; accepted 18 April 1998

ABSTRACT: Measurements were made of the relaxation of the stress of stretched polypropylene (PP) and ethylene-propylene-diene elastomer blend vulcanizates at various strain levels. It was found that PP-blended vulcanizates showed greater relaxation than that of the gum vulcanizate at all extensions. There was a continual increase in the relaxation rate with the 10% PP-blended vulcanizate but an initial sharp decrease and then a flattening tendency with the above 10% PP-blended vulcanizate at an increasing stain level. An interesting observation of the study was that the rate of stress relaxation decreased linearly in two steps in the case of blend vulcanizates above 10% PP at 100% and above strain levels. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2155–2162, 1998

Key words: relaxation of the stress; polypropylene (PP); ethlene–propylene–diene elastomers; strain labels

INTRODUCTION

In recent years, the approach of the development of a new polymer from the blending of the two or more polymers has gained importance among polymer scientists. Within the scope of the blending of polymeric materials, various blends can be achieved: plastomer-elastomer, plastomer-plastomer, and elastomer-elastomer. The polymeric system, namely, ethylene-propylene-diene elastomer terpolymer (EPDM)-polypropylene (PP), was chosen for the present study. PP is a typical heat-resistant plastomer and EPDM is a highimpact resistant elastomer. From these two requrements, different families of EPDM-PP were born. Various scientific reports and patents¹⁻⁹ created the technical background and essential knowledge to enhance end-use development of EPDM–PP blends. All the above works on EPDM–PP blends were confined to studies on thermoplastic elastomers.

The result shows poor elastic behavior at increasing temperature. Weak intermolecular binding forces are the main factor responsible. The possible theoretical ways to prevent or reduce the viscous creep under strain are a polar modification of the olefinic chains or providing a certain degree of crosslinking between EPDM molecules themselves and, if possible, between EPDM and PP as well. Several researchers have carried out, published, and patented experiments involving crosslinking of the elastomeric component. Fischer^{10,11} worked on blending PP with EPDM given some degree of crosslinking. The techniques based on carrying out both the blending and crosslinking reaction in one stage (dynamic cure blending) were studied by many workers.¹²⁻¹⁴ Gessler and Haslett¹² showed that after dynamic curing the material was thermoplastic in nature. Coran et al.^{13,14} prepared a fully cured EPDM–PP

Correspondence to: B. B. Konar.

Journal of Applied Polymer Science, Vol. 70, 2155–2162 (1998) © 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/112155-08

Ingredients	Gum	A_1	A_2	A_3	A_4	A_5
EPDM	100.00	100.00	100.00	100.00	100.00	100.00
PP	0	11.11	25.00	42.86	66.67	100.00
Zinc oxide	5.00	5.00	5.00	5.00	5.00	5.00
Stearic acid	1.20	1.20	1.20	1.20	1.20	1.20
Sulfur	2.00	2.00	2.00	2.00	2.00	2.00
MBTS	2.50	2.50	2.50	2.50	2.50	2.50
TMT	0.50	0.50	0.50	0.50	0.50	0.50
Total	111.20	122.31	136.20	154.06	177.87	211.20
EPDM : PP	100 : 0	90 : 10	80 : 20	70:30	60 : 40	50 : 50

Table I Formula for Experimental Compounds

composite by dynamic vulcanization and referred to it as a thermoplastic vulcanizate which has unique properties in many respects. However, it appears that no systematic studies have been reported for two-stage processes (static vulcanization) as done for normal elastomer vulcanization. Our attempt was to study the two-stage vulcanizate of the EPDM-PP blend. The present work was undertaken to study the stress relaxation of the EPDM-PP blend vulcanizate. Stress-relaxation properties assume importance in view of the increasing use of polymer-elastomer blends in many products like hoses, belts, cables, and gaskets. In this article, the results of our studies on the stress relaxation of EPDM-PP are reported with the objectives of studying the effect of the strain level and behavior of the blends at different relative volumes of PP.

EXPERIMENTAL

Materials

The EPDM rubber (Royalene 301T; DCPD polymer, nonstaining, from the Uniroyal Chemical Co., Naugatuck, CN) used had a Mooney viscosity ML_{1+4} (125°C) of 40, a specific gravity of 0.87 and an E/P ratio 68/32. The PP (EBI 0830; IPCL, Vadodara, India) used has an MFI of 0.8. The other compounding ingredients were from standard sources.

Sample Preparation and Testing

Formulation of the mixes are shown in Table I. The recipes differed only in the dose of PP. The blends were prepared in different stages. The mastication of EPDM was done in a baby two-roll mill (150×330 mm) in its cold condition. PP was then mixed at a temperature about 60°C. The mixes were then passed through a laboratory-size extruder at 180°C and, finally, the blends were compounded with other ingredients [zinc oxide, stearic acid, sulfur, mercaptobenzothiazyl disulfide (MBTS), and tetramethylthiuram disulfide (TMT)] according to ISO 2393. The mixes were vulcanized to their optimum cure times, as determined by a Monsanto rheometer R-100. Sheets 2 mm thick were molded at 170°C and 4.5 MPa pressure in an electrically heated press. Dumbbell specimens (ASTM D412; type C) were



Figure 1 Stress-relaxation curves for EPDM gum vulcanizate. Successive graphs are displaced upward by 0.1 for clarity. Figures against lines indicate strain (%).

Strain (%)	Slope (Negative)			Intercept at 1s			Contribution	Intersection
	Early	Later	Difference	Early	Later	Difference	of Early Process (%)	Point on Time Axis (s)
25	0.0483	_	_	0.9866	_	_	_	_
50	0.0454	_		0.9866	_	_	_	_
75	0.0464	_		0.9800	_	_	_	—
100	0.0428	_		0.9800	_	_	_	_
125	0.0411	—	_	0.9800	—	—	—	_

Table II Results of Stress-Relaxation Measurements for Gum Vulcanizate

punched out of these sheets. To measure the stress relaxation, an Instron tester (Model 4301) was used to elongate the samples to the desired length, at a crosshead speed of 0.041 cm s⁻¹. Special clamps, provided with a spring action, were used. These clamps kept the specimen from slipping during elongation. In all cases, three specimens were tested and average values reported. All tests were carried out at room temperature, about 25°C. Extensions used were 25, 50, and 75% and up in steps of 50% until break.

RESULTS AND DISCUSSION

Linear plots were obtained when S_t/S_0 is plotted against log t (Fig. 1) for gum samples of EPDM at



Figure 2 Stress-relaxation curves for mix A_1 . Successive graphs are displaced upward by 0.1. Symbols on the lines indicate strain (%).

 A_1, A_2, A_3, A_4 , and A_5) are shown in Figures 2–6, respectively. The experimental points for the blend A_1 (10% PP) show single straight lines as 1.0 1.0 1.0 1. 1.0 250 1.0 St/So 00 1.0 1.0 0,9 0.8 0.7 0.6 10⁰ 10² 10³ 104 10 TIME (sec)

five strain levels (S_0 is obtained from the maximum load at t = 0 when the desired strain is

reached; S_t is the stress at subsequent time t).

The slopes and intercepts vary little with strain level (see Table II). These results are in agree-

ment with those reported by Gent¹⁵ for natural

rubber, by Voit et al.¹⁶ for styrene-butadiene

(SBR), butyl, and polybutadiene rubbers, and by

The results of the EPDM and PP blends (mixes

De et al.¹⁷ for nitrile rubber.

Figure 3 Stress-relaxation curves for mix A_2 . Successive graphs are displased upward by 0.1. Symbols on the lines indicate strain (%).



Figure 4 Stress-relaxation curves for mix A_3 . Successive graphs are displaced upward by 0.1. Symbols on the lines indicate strain (%).

for gum vulcanizate. For other blend systems, the experimental points show two different patterns: (i) below 100% strain level, single straight lines, and (ii) above 100% strain level, two straight lines are found for each strain level. Like gum vulcanizate, the slopes and intercept of the " A_1 mix" vary little with the strain level (see Table III). For other mixes, the slopes and intercepts are shown in Tables IV–VII. At higher strain level, the first line is of a greater slope and applies for short times (<600 s), and the second line, for longer times. Similar results were obtained by Mackenzie and Scanlan¹⁸ for carbon black-filled vulcanizates.

The present experimental results show that the incorporation of PP on and above 20% loading results in two relaxation processes at high strain levels (100% and above). The experimental data of the EPDM and PP-blend vulcanizates on and above 20% loading at 100% and above strain levels may be characterized by four parameters: Two slopes and corresponding intercepts on the ordinate at 1S. The values are shown in Tables II-VII for different strain levels for gum and other mixes. The result shows that in all cases the earlier slope is greater than the later one. It is seen that there is a gradual decrease with extension in the relaxation rate in the gum. It is known that stress relaxation in an unfilled vulcanizate is determined by a number of elementary processes such as chain motion and orientation, rearrangement of broken chains, crosslinks, and entanglements.^{15,19,20,21} In some elastomers, crystallization plays an important part.¹⁵ In a noncrystallizing gum such as EPDM, the rate of stress relaxation decreases with elongation. This behavior arises from the limited extensibility of the chains in the network. Partly extended chains can rearrange themselves readily, but fully extended chains are incapable of major adjustments. The number of fully extended chains increases with the imposed extension; therefore, an increasing portion of the network will cease to contribute to



Figure 5 Stress-relaxation curves for mix A_4 . Successive graphs are displaced upward by 0.1. Symbols on the lines indicate strain (%).



Figure 6 Stress-relaxation curves for $mix A_5$. Successive graphs are displaced upward by 0.1. Symbols on the lines indicate strain (%).

stress relaxation. The PP-loaded vulcanizates have a higher degree of relaxation than has the corresponding gum vulcanizate at almost all extensions. Gent¹⁵ showed that the presence of a crystalline phase leads to an increased relaxation of the stress. It was reported that an improved stress-distribution mechanism in the oriental crystallite, linking a number of elastomer chains together, is responsible for the increase in relaxation rate.²²⁻²⁴ The result shows that with 10%

PP-loaded vulcanizate there is a continual increase in the relaxation rate. But there is a sharp earlier decrease and later it tends to be flatter with an increasing strain level for higher PP-loaded vulcanizate. It is known that there are weak interactions (only physical bonding) between EPDM chains and PP chains (with the limited alignment of PP chains). These results are in agreement with those reported by Voet et al. 25

A method¹⁸ of estimating the contribution of the early mechanism to the relaxation in the system is to divide the difference of the intercept of the two lines by the intercept of the first line at t = 1 s. This fraction, expressed as a percentage, is also shown in Tables II-VII. From the tables, it is seen that the contribution of the early process is nearly constant in the case of the $A_2 \min (4\%)$, decreases with the strain level from 8 to 2% in the A_3 mix and from 12 to 4% in A_4 mix, but increases with strain level from 3 to 9% in the A_5 mix. This indicates better bonding at the plastomer/elastomer interface in the A_2 mix than in other mixes.

Furthermore, it may be noted that the time of the intersection of the two lines is approximately constant (about 300 s) for A_2 , but it varies from 200 to 450 s for A_3 and A_4 and from 300 to 600 s for A_5 . The values shown in Tables II–VII represent the change over time at which the mechanism operating at the previous process becomes exhausted.

Table VIII shows the effect of PP concentration (gum and other mixes) on the stress-relaxation values at 100% strain level. The rate of relaxation increases with PP content. The contribution of the early process increases to the 30% PP mix and then decreases and is lowest at the 50% mix. The time at which the earlier relaxation mechanism is exhausted shifts to higher values. According to

(s)

Strain (%)	Slope (Negative)				Intercept a	at 1 <i>s</i>	Contribution	Intersection
	Early	Later	Difference	Early	Later	Difference	of Early Process (%)	Point on Time Axis (s)
25	0.0333	_	_	0.9666	_	_	_	_
50	0.0340	_	_	0.9733	_	_	_	
75	0.0407	_	_	0.9733	_	_	_	_
100	0.0444	_	_	0.9800	_	_	_	_
150	0.0428	_	_	0.9733	_	_	_	
200	0.0454	_	_	0.9800	_	_	_	_
250	0.0476	_	_	0.9733	_	_	_	_

Table III Results of Stress-Relaxation Measurements for A, Mix Vulcanizate

Strain (%)	S	Slope (Nega	tive)	Iı	ntersection	at 1s	Contribution	Intersection
	Early	Later	Difference	Early	Later	Difference	of Early Process (%)	Time Axis (s)
25	0.0483	_	_	0.9800	_	_		
50	0.0592		_	0.9800		_	_	_
75	0.0551		_	0.9733		_	_	_
100	0.0555	0.0454	0.0101	0.9800	0.9406	0.0394	4.02	392
150	0.0571	0.0400	0.0171	0.9733	0.9340	0.0393	4.04	337
200	0.0607	0.0366	0.0241	0.9666	0.9274	0.0392	4.05	290
250	0.0500	0.0322	0.0178	0.9666	0.9274	0.0392	4.05	290
300	0.0483	0.0348	0.0135	0.9666	0.9274	0.0392	4.05	268
350	0.0538	0.0368	0.0170	0.9600	0.9208	0.0392	4.08	268
400	0.0500	0.0375	0.0125	0.9533	0.9208	0.0325	3.41	249

Table IVResults of Stress-Relaxation Measurement for A_2 Mix Vulcanizate

the theory of strain amplification,²⁶ owing to the inextensibility of the filler, the strain in the elastomer matrix is greater than the overall strain, resulting in the rubber phase having an instan-

taneous modulus higher than for a gum rubber at an equivalent extension. In relating strain amplification to stress relaxation, $Derham^{27}$ showed that the stress-relaxation rate increases with car-

Table V	Results of	f Stress-Relaxation	Measurements	for A_3	Vulcanizate
---------	-------------------	---------------------	--------------	-----------	-------------

Strain (%)	S	Slope (Nega	tive)		Intercept a	t 1s	Contribution	Intersection
	Early	Later	Difference	Early	Later	Difference	of Early Process (%)	Time Axis (s)
25	0.1149	_	_	0.9934	_	_	_	_
50	0.1079		_	0.9866		_	—	_
75	0.1016		_	0.9866		_	—	_
100	0.1000	0.0707	0.0293	0.9866	0.9142	0.0724	7.34	457
150	0.0756	0.0562	0.0194	0.9800	0.9208	0.0592	6.04	423
200	0.0689	0.0522	0.0167	0.9733	0.9274	0.0459	4.72	337
250	0.0773	0.0516	0.0257	0.9733	0.9406	0.0327	3.36	268
300	0.0765	0.0654	0.0111	0.9666	0.9406	0.0260	2.69	214
350	0.0720	0.0560	0.0160	0.9666	0.9208	0.0458	4.74	198
400	0.0708	0.0571	0.0137	0.9600	0.9274	0.0326	3.39	184

Table VI	Results of Stress-Rela	axation Measurements :	for A ₄ Mix Vulcanizate
----------	-------------------------------	------------------------	------------------------------------

Strain (%)	S	Slope (Nega	tive)		Intercept a	t 1s	Contribution	Intersection
	Early	Later	Difference	Early	Later	Difference	of Early Process (%)	Time Axis (s)
25	0.1187	_	_	0.9462	_	_	_	_
50	0.1181		_	0.9924		_	_	_
75	0.1111		_	0.9792		_	_	_
100	0.0947	0.0812	0.0135	0.9924	0.9330	0.0594	6.36	493
150	0.1000	0.0692	0.0308	0.9858	0.8924	0.0934	10.46	364
200	0.1125	0.0750	0.0375	0.9792	0.8792	0.1000	11.37	231
250	0.0933	0.0720	0.0213	0.9792	0.9132	0.0660	7.22	198
300	0.1166	0.0777	0.0389	0.9726	0.9132	0.0594	6.50	170
350	0.1067	0.0777	0.0290	0.9792	0.9264	0.0528	5.69	146
400	0.1000	0.0888	0.0112	0.9660	0.9264	0.0396	4.27	135

	Slope (Negative)				Intercept a	t 1 <i>s</i>	Contribution	Intersection	
Strain (%)	Early	Later	Difference	Early	Later	Difference	of Early Process (%)	Point on Time Axis (s)	
25	0.1513	_	_	0.9866	_	_		_	
50	0.1483	_	_	0.9857		_	_	_	
75	0.1218	_	_	0.9868			_	_	
100	0.1428	0.1100	0.0328	0.9858	0.9538	0.0320	3.24	600	
125	0.1357	0.1200	0.0157	0.9660	0.9208	0.0452	4.68	464	
150	0.1384	0.0923	0.0461	0.9726	0.9000	0.0726	7.46	464	
175	0.1400	0.0903	0.0497	0.9660	0.8284	0.1376	14.24	501	
200	0.1273	0.0800	0.0473	0.9396	0.8284	0.1112	11.83	398	
300	0.1111	0.0818	0.0293	0.9528	0.8746	0.0782	8.21	316	

Table VII Results of Stress-Relaxation Measurements for A5 Mix Vulcanizate

bon black loading. Similar results are obtained in the EPDM–PP blend vulcanizate as shown in Table VIII.

CONCLUSIONS

The main conclusions can be summarized as follows:

- 1. In the gum vulcanizate of EPDM, there is initially a decline in the rate of stress relaxation at increasing elongation, followed by a constant rate at higher extensions.
- 2. In the 10% PP mix, the EPDM vulcanizate strain level is above 125%, and alignment of the persistent PP chains and rupture of the elastomer/plastomer bonds cause the increase in the relaxation rates.
- 3. At higher loading, reestablishing of the broken bonds is not possible in view of the dissimilar strain-magnification effect

caused by the presence of a more or less elongating plastomer fraction.

4. The existence of a relaxation mechanism is observed at times near 600 s in the polypropylene/ethylene propylene diene blends. This is evident from the existence of two linear sections in the plot of stress versus the logarithmic time.

REFERENCES

- 1. C. Shih, U.S. Pat. 3,888,949 (1973).
- 2. A. Fritz and C. Shih, U.S. Pat. 3,882,197 (1973).
- 3. W. K. Fischer, U.S. Pat. 3,835,201 (1972).
- G. A. Von Booungen and C. L. Meredith, U.S. Pat. 3,957,919 (1974).
- H. L. Morris, J. Elastom. Plast., 6, 1 (1974); U.S. Pat. 4,031,169 (1977).
- 6. W. K. Fischer, Mod. Plast., 51, 50 (1974).
- 7. W. K. Fischer, Mat. Energy Ind., 2(3), 18 (1975).
- 8. P. T. Stricharczuk, U.S. Pat. 4,036,912 (1977).
- C. J. Carman, M. Batiuk, and B. M. Harman, U.S. Pat. 4,046,514 (1977).

Table VIII Effect of PP Concentration on Stress-Relaxat	on Properties
---	---------------

	~ .	S	lope (Nega	ative)	Ir	tersection	at 1s	Contribution of Early Process (%)	Intersection
	Strain (%)	Early	Later	Difference	Early	Later	Difference		Point on Time Axis (s)
G	100	0.0428	_	_	0.9800	_	_		_
A_1	100	0.0444		_	0.9800		_	_	
A_2	100	0.0555	0.0454	0.0101	0.9800	0.9406	0.0394	4.02	392
$\tilde{A_3}$	100	0.1000	0.0707	0.0293	0.9866	0.9142	0.0724	7.34	457
A_4	100	0.0947	0.0812	0.0135	0.9924	0.9330	0.0594	6.36	493
A_5	100	0.1428	0.1100	0.0328	0.9858	0.9538	0.0320	3.24	600

- 10. W. K. Fischer, Rubb. World, 49 (1973).
- 11. W. K. Fischer, U.S. Pat. 3,806,558 (1974).
- 12. A. M. Gessler and W. H. Haslett, U.S. Pat. 3,037,954 (1962).
- A. Y. Coran, B. Das, and R. P. Patel, U.S. Pat. 4,130,535 (1978).
- A. Y. Coran and R. P. Patel, *Rubb. Chem. Technol.*, 53, 141 (1980); 54, 91 (1981).
- A. N. Gent, Rubb. Chem. Technol., 36, 337, 389 (1963).
- A. Voet, A. K. Sarcar, and F. R. Cook, *Rubb. Chem. Technol.*, 44, 185 (1971).
- S. S. Bhagawan, D. K. Tripathy, and S. K. De, J. Appl. Polym. Sci., 33, 1623 (1987).
- C. I. Mackenzie and J. Scanlan, J. Polym., 25, 559 (1985).
- 19. G. M. Barlenev and N. M. Lyalina, *Plasteukautschuk*, 11, 835 (1969).

- P. Thirion and R. Chasset, *Rubb. Chem. Technol.*, 37, 617 (1964).
- A. V. Tobolsky, Properties and Structure of Polymers, Wiley, New York, 1960, Chap. V.
- 22. R. S. Stein and R. S. Finkelstein, Annu. Rev. Phys. Chem., 207 (1973).
- G. L. Wilkes, J. Macromol. Sci. Rev. Macromol. Chem. C, 10, 149 (1974).
- C. B. Wang and S. L. Cooper, in *Polymer Blends* and *Composites in Multiphase System*, C. D. Han, Ed., American Chemical Society, Washington, DC, 1984, Chap. 8.
- 25. A. Voet, A. K. Sircar, and T. J. Mullens, *Rubb. Chem. Technol.*, **42**, 874 (1969).
- L. Mullins and V. R. Tobin, in *Proceedings 3rd Rubber Technology Conference*, London, 1954, p. 397.
- 27. C. J. Derham, J. Mater. Sci., 8, 1023 (1973).