Dynamically Vulcanized Nitrile Rubber/Polyoxymethylene Thermoplastic Elastomers

XIANGFU ZHANG, YONG ZHANG, ZONGLIN PENG, XIUYONG SHANG, YINXI ZHANG

Polymeric Materials Research Institute, Shanghai Jiao Tong University, Shanghai 200240, China

Received 14 September 1999; accepted 30 October 1999

ABSTRACT: A new type of oil-resistant thermoplastic elastomer of nitrile rubber (NBR) and polyoxymethylene (POM) prepared by dynamic vulcanization were studied. The effects of the curing systems for NBR, acrylonitrile content in NBR, POM content, thermal aging, and reprocessing have on the mechanical properties of NBR/POM thermoplastic elastomers were investigated in detail. NBR/POM thermoplastic elastomers have high tensile strength and excellent oil resistance at elevated temperature. NBR/POM thermoplastic elastomers can be produced in a wide range of hardness. NBRs with higher acrylonitrile content are more suitable for preparing NBR/POM thermoplastic elastomer with high tensile strength and good oil resistance. The NBR/POM thermoplastic elastomer has significantly improved electrical insulation properties compared with NBR (Gessler, M. U.S. Pat. 3,037,954, 1962). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2641–2645, 2000

Key words: NBR; POM; TPE; dynamical vulcanization; mechanical properties

INTRODUCTION

Dynamic vulcanization was first discribed by Gessler[1] in 1962 and then developed by Fisher,[2] and Coran et al.[3,4] Some thermoplastic elastomers (TPE) through dynamic vulcanization have been commercialized with trade names such as Santoprene and Geolast, etc.

Nitrile rubber (NBR) is well known for its good oil resistance,[5] but its ozone resistance and electrical insulation properties are relatively poor. To overcome the disadvantages, NBR is usually blended with plastics such as polyvinyl chloride, polyamide, polyurethane, and polypropylene (PP).[6–9] There are few publications concerning polyoxymethylene (POM)/NBR blends.

In this article, an oil-resistant TPE prepared by dynamic vulcanization of POM and NBR blend is reported for the first time. The effects of curatives, acrylonitrile (AN) content in NBR, and POM/NBR ratio on the properties of dynamically vulcanized NBR/POM blends were studied in detail.

EXPERIMENTAL

Raw Materials

POM (melt flow index 6.0) was produced in the Shanghai Solvent Factory in China. Butadiene rubber (BR), nitrile rubbers of NBR-18 and NBR-40 with AN content 18 wt % and 40 wt % are the products of the Lanzhou Chemical Co. in China. The other nitrile rubbers (N241, N230S, and N220S) are the products of Japan Synthetic Rubber Co.

NBRs with varied AN content of 26, 33, and 40 wt % used in this work may be divided into two groups: one is self-curable at elevated tempera-

Correspondence to: X. Zhang, Shanghai Pret Institute of Chemistry, Shanghai 200092, China.

Journal of Applied Polymer Science, Vol. 77, 2641–2645 (2000)

Table I Effect of Peroxides

Peroxide Type	DMDTPH	DCP
Hardness (shore A)	90	87
100% modulus (MPa)	9.70	9.48
Tensile strength (MPa)	15.67	13.92
Elongation at break (%)	240	210
Tension set at break (%)	26	25

Formulation: NBR-40 100, POM 50, peroxide 1.0, sulphur 0.1.

Table II Effect of the Peroxide Content on the Properties of NBR-40/POM TPE

DMDTPH (phr)	0	0.5	1.0	2.0
Hardness (shore A)	82	86	90	92
Tensile strength (MPa)	11.2	13.9	14.9	10.2
Elongation at break (%)	242	240	215	91
Tension set at break (%)	32	29	33	10
Insoluble content of NBR (%)	80.6	93.4	96.6	97.5

Formulation: NBR-40 100, POM 50, peroxide 1.0, sulphur 0.1.

tures in the absence of any curative, the other is non–self-curable. To determine whether a rubber is self-curable, an NBR rubber was mixed at 200°C. Self-curable rubbers could generally jell and crumble within 2 to 8 min, whereas non–self-curable rubbers could be mixed over 20 min without crumbling. The results showed that NBR-40 is a self-curable rubber and the remainder are non–self-curable.

Basic Composition

The basic formulation is listed as follows: NBR-40 100, POM variable, stearic acid 1.0, antioxidant Irgnox-259 0.5, *N*-cyclohexyl-*N*-phenyl-*p*-phenylene diamine 1.0, 2,5-dimethyl-2,5-di(*t*-butylperoxy) hexane 1.0, sulfur 0.1 phr.

Preparation of TPE

NBR stocks consisting of NBR, zinc oxide, stearic acid, and a curing agent were first prepared on a two-roll mill at room temperature. The preparation of NBR/POM TPE was performed at 180°C in the mixer of a XSS-300 torque rheometer. Three minutes after melting of POM resin in the mixer, NBR stocks were added into the mixer. Five minutes after the maximum torque occurred, the composition was removed from the mixer, and immediately passed through a cold twin-roll mill to give a 2-mm sheet. The sheet was cut into small pieces that were remelted and mixed for 2 min in the mixer. The procedure was repeated again to obtain a 2-mm sheet. The sheet was then compression-molded in a press at 190°C, then cold pressed to give samples for testing.

Measurement

The tensile properties and tear strength of NBR/POM TPE were measured according to the Chinese Standard GB527-83. Shore A hardness was recorded in 5 s after presser foot contacted the sample. Oil resistance of the TPE was measured at 100°C for 3 days in the mixed solvent of 50 vol % high boiling point paraffin oil and 50 vol % xylene. Gel content was measured in acetone at 100°C for 24 h and calculated on the NBR content. The apparent viscosity of TPE was measured with a capillary rheometer at 200°C. The length/diameter ratio (L/D) of capillary is 40. On the viscosity and shear rate data, Rabinowitsch corrections were applied.

Table III Effect of Sulphur Content on the Properties of NBR/POM TPE

Sulfur Content (phr)	0	0.1	0.3	0.5
Hardness (shore A)	91	90	87	87
Tensile strength (MPa)	12.1	14.9	15.6	13.8
Elongation at break (%)	142	215	238	244
Tension set at break (%)	14	33	32	28
Insoluble content of NBR in acetone at 100°C for 24 h (%)	97	97	94	93

Formulation: the basic formulation, POM 50, sulphur variable.

Table IV Effect of AN Content in NBR on the Properties of NBR/POM TPE

AN Content of NBR	0	18	26	35	40
Solubility Parameter $(KJ/m^3)^{1/2}$	8.1	8.7	9.38	9.64	10.3
Hardness (shore A)	77	88	90	91	88
Tensile strength (MPa)	3.3	5.1	10.1	12.1	12.5
Elongation at break (%)	60	105	132	164	197
Tension set at break (%)	4	4	12	16	18

Formulation: the basic formulation, POM 50, NBR variable.

RESULTS AND DISCUSSION

Effect of Peroxides and Coagents

The effect of peroxides as curatives on the properties of NBR/POM TPE is complicated to some degree because the NBR-40 tends to be self-cured at elevated temperature. As shown in Table I, the NBR/POM TPE cured with 2,5-dimethyl-2,5-*di*(*t*-butylperoxy) hexane (DMDTPH) has higher tensile strength than that with dicumyl peroxide (DCP). DCP has a lower decomposition temperature and a shorter half-life of decomposition at a given elevated temperature than DMDTPH, which may account for the difference shown by using the two peroxides.

The effect of the DMDTPH content on the properties of NBR/POM TPE is shown in Table II. The addition of the peroxide into NBR/POM TPE led to the increase in tensile strength of NBR/POM TPE and the promotion of the gel content. However, the overloading of peroxide is not necessary for the preparation of NBR/POM TPE, which results in the decomposition of POM and consequently injures the mechanical properties of NBR/POM TPE.

It is well known that polypropylene (PP) degrades in the presence of peroxide at elevated temperature, and it has been reported that the degradation of PP could be inhibited by the addition of a small amount of sulphur.[9] In our study, sulphur was found to be effective for the inhibition of degradation of POM in the presence of peroxide at elevated temperature just like sulphur in PP. The torque shown in the Haake rheometer was approximately 6.5 $N \cdot$ m for POM melt at 180°C; it dropped to 5.5 $N \cdot$ m after adding peroxide DMDTPH, indicating the apparent degradation of POM. As shown in Table III, a small amount of sulphur is suitable for preparing NBR/POM TPE without showing apparent degradation of POM, and the overloading of sulphur impairs the tensile strength of NBR/POM TPE and decreases the gel content.

Effect of AN Content in NBR

The AN content in NBR has a great effect on the properties of NBR/POM TPE as shown in Table

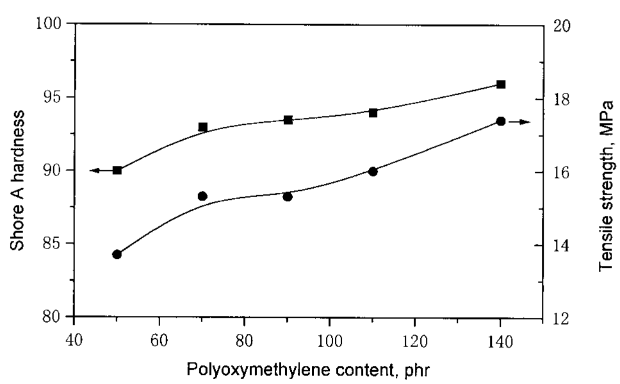

Figure 1 Effect of POM content on the mechanical properties of NBR-40/POM TPE.

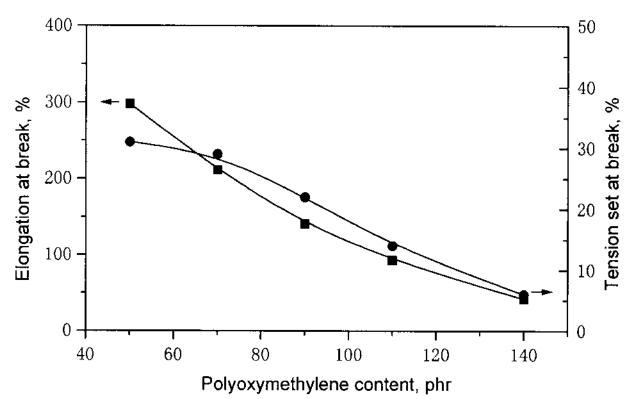

Figure 2 Effect of POM content on the mechanical properties of NBR/POM TPE.

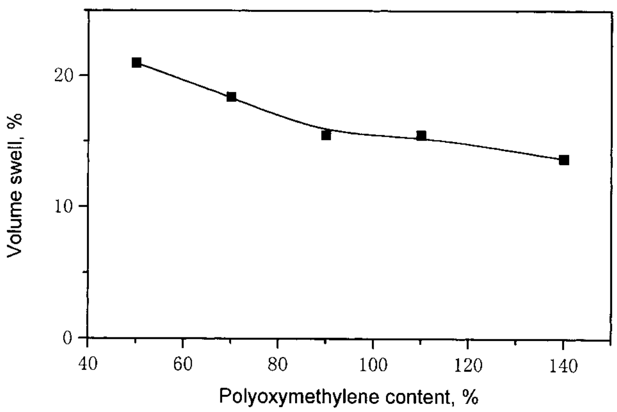

Figure 3 Effect of POM content on the oil resistance of NBR-40/POM TPE.

Table V Aging Resistance of NBR-40/POM Blend (Aging at 120°C for 72 h)

POM Concentration (phr)	50	70	90	110	140
Change of hardness (shore A)	+1	0	+1	+1	+1
Retention of tensile strength (%)	68.2	68.6	89.0	75.6	75.6
Retention of elongation at break (%)	70.4	63.2	66.0	82.5	50.0

Formulation: the basic formulation.

IV. It may be explained by the compatibility between POM and NBR with varied AN content. The solubility parameter of NBR-40 which has the highest AN content is closest to that of POM (10.5), and their blend has the best properties among all the blends of POM and NBR.

Effect of POM Content

The effect of POM content on the properties of NBR/POM TPE is showned in Figs. 1–3. With increasing the POM content, the tensile strength and hardness of the TPE increases, and the elongation at break decreases. The tension sets at break of all of the TPE are less than 50%, which relates to the low elongations at break of NBR/POM TPE. With increasing the POM content, the volume swell of the TPE in the mixed solvent of 50 : 50 high boiling paraffin oil and xylene at 100°C decreases, indicating the presence of POM in TPE improves the oil resistance.

Table V shows the aging resistance of the POM/NBR TPE. All the TPEs with POM content varied from 50 to 140 phr exhibit the high retention of tensile strength and elongation at break after aging, indicating NBR/POM TPE has good aging resistance.

Table VI shows the effect of POM content on the electrical properties of NBR/POM TPE. In contrast to NBR which has very low volume electrical resistivity and dielectric strength, the NBR/POM TPE has significantly improved electrical properties. The higher the POM content, the higher the volume resistivity and dielectric strength, and the lower the dielectric constant of the TPE. It is evident that the NBR/POM TPE can be used as a good electrical insulation material.

Effect of Reprocessing

An important advantage of TPE over the conventional thermosetting rubbers is that TPE can be reprocessed by all common equipment for plastics processing, such as extruders, injection molders, and blow molders without significantly changing the physical properties of TPE. To illustrate this reprocessing ability of the NBR/POM TPE, the TPE is reprocessed five times by compression

Table VI Effect of POM on the Electrical Properties NBR/POM TPE Cured by Peroxide

NBR Content	100	100	100	100	100	100	0
POM content	0	50	70	90	110	140	100
Volume resistivity (10^8 Ω · m)	0.0035	26.5	17.5	16.4	237	276	10000
Dielectric strength (KV/mm)	9.83	20.3	28.3	28.6	27.8	27.2	47.2
Dielectric constant	13	11.5	10.1	9.4	9.3	7.8	3.8

Formulation: the basic formulation.

molding with the product being reground after each molding cycle. The tensile properties and rheological behavior were measured after each cycle, as shown in Figures 4 and 5. It was found that the tensile strength and elongation at break of the TPE decrease somewhat after reprocessing. This may be attributed to the slight degradation of POM, which was evidenced by the decreasing of apparent viscosity of the TPE after reprocessing.

CONCLUSIONS

A new type of oil-resistant TPE of NBR and POM was prepared by dynamic vulcanization. The curing systems, acrylonitrile content in NBR, POM content, and reprocessing have effects on the mechanical properties of NBR/POM thermoplastic elastomer. NBR/POM TPEs have high tensile strength and excellent oil resistance at elevated temperature. NBR/POM TPEs can be produced in a wide range of hardness. NBR with higher AN content are more suitable for preparing NBR/POM TPE with high tensile strength and good oil resistance. The NBR/POM TPE has significantly improved electrical insulation properties compared with NBR.

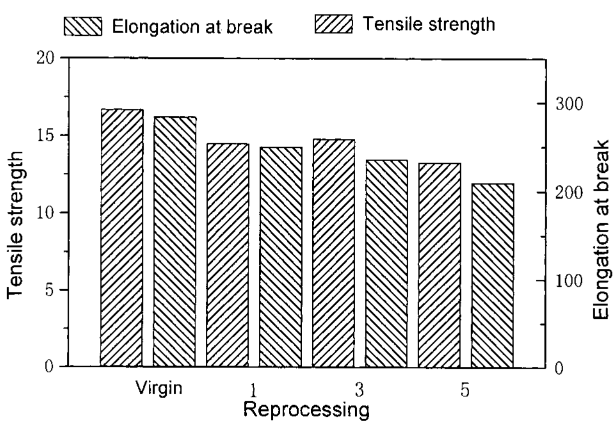

Figure 4 Retention of tensile properties of reprocessed NBR-40/POM (100 : 50) TPE.

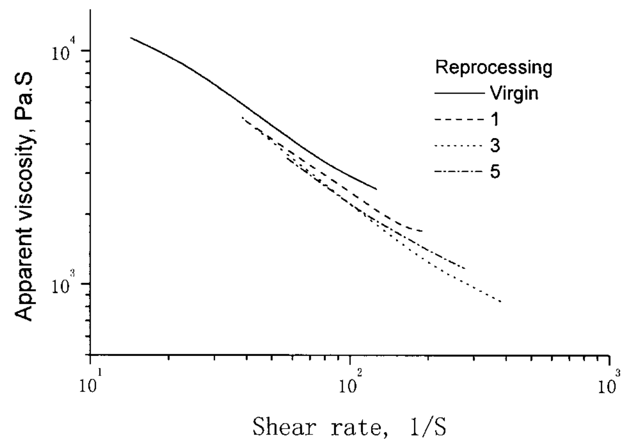

Figure 5 Rheological properties with reprocessed NBR-40/POM (100/50) TPE.

REFERENCES

1. Gessler, M. U.S. Pat. 3,037,954, 1962.
2. Fisher, K. U.S. Pat. 3,758,643, 1973.
3. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 1980, 53, 141.
4. Coran, A. Y.; Patel, R. P.; Williams, D. Rubber Chem Technol 1982, 55, 117.
5. Blow, M. Rubber Technology and Manufacture; Plastics and Rubber Institute: London, 1978; p. 119.
6. Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum Press: New York, 1976; p. 87.
7. Coran, A. Y.; Pate, R. Rubber Chem Technol 1983, 56, 1045.
8. Tang, T.; Hu, C. P.; Yin, S. K.; Zhang, Y. X. Adv Polym Blends Alloys Technol 1993, 4, 1.
9. Zhang, X. F.; Hong, D. W.; Zhu, Y. T.; Zhang, Y. X. Xiangjiao Gongye (Chinese), 1993, 40, 452.