

Dynamically Vulcanized Nitrile Rubber/Polypropylene Thermoplastic Elastomers

XIANGFU ZHANG, HUA HUANG, YINXI ZHANG

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 30 May 2001; accepted 28 August 2001

ABSTRACT: A new compatibilized method was used to prepare thermoplastic elastomer (TPE) of nitrile rubber (NBR) and polypropylene (PP) with excellent mechanical properties by dynamic vulcanization. Glycidyl methacrylate (GMA) grafted PP/amino-compound was used as a compatibilizer. The effects of the curing systems, compatibilizer, PP type, and reprocessing on the mechanical properties of NBR/PP thermoplastic elastomers were investigated in detail. Experimental results showed that the addition of amino-compound in the compatibilizer can significantly increase the mechanical properties of the NBR/PP thermoplastic elastomer. Compared with other amino-compounds, diethylenetriamine (DETA) has the best effect. PP with higher molecular weight is more suitable for preparing NBR/PP thermoplastic elastomer with high tensile strength and high elongation at break. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2862–2866, 2002

Key words: mechanical properties; vulcanization; rubber; polypropylene; thermoplastics; elastomers

INTRODUCTION

Dynamic vulcanization was first described by Gessler¹ in 1962 and then developed by Fisher² and Coran et al.³ Some thermoplastic elastomers (TPE), through dynamic vulcanization, have been commercialized with trade names such as Santoprene, Geolast, etc.

Nitrile rubber (NBR) is well known for its good oil resistance, but its ozone resistance and electrical insulation properties are relatively poor. To overcome these disadvantages, NBR has been blended with plastics such as polyvinyl chloride, polyamide, polyurethane, polyoxymethylene, and polypropylene.^{4–8}

Blending of immiscible polymers offers attractive opportunities for developing new materials

with useful combinations of properties. However, most blends are immiscible, and often have poor mechanical properties and unstable morphologies. Compatibilization of such blends is necessary.

NBR/PP is typically immiscible in blends.^{9–12} To achieve NBR/PP TPE with practical value, addition of suitable PP–NBR block copolymers, or the generation of these copolymers *in situ* during the melt blending, was adopted. Coran et al.^{6–8} did much work in this field and proposed several ways for achieving PP–NBR block copolymers, such as: (1) using peroxide directly; (2) halogenation; (3) PP functionalized with maleic anhydride (MAH-*g*-PP) reacts with amino-terminated NBR; (4) MAH-*g*-PP reacts with NBR containing a carboxyl group; (5) with Lewis acid existing, adding *t*-butyl phenolic resin to react with PP and amino-terminated NBR; (6) using *t*-butyl phenolic resin to modify PP and then react with amino-terminated NBR.

Correspondence to: X. Zhang (xfzhang@maill.sjtu.edu.cn).

Journal of Applied Polymer Science, Vol. 85, 2862–2866 (2002)
© 2002 Wiley Periodicals, Inc.

Usually, no significant compatibilizing effect was obtained when only MAH-*g*-PP was used as the compatibilizer. This is due to low reactivity of NBR and less NBR-PP block copolymer being formed. Adding a small amount of amino-terminated NBR will lead to reaction with MAH-*g*-PP and formation of NBR-PP block copolymers *in situ*. The TPEs through dynamic vulcanization, with trade names such as Geolast, aret obtained by this kind of compatibilizer. However, most reports describe use of MAH-*g*-PP as the compatibilizer in NBR/PP TPE. There is no publication concerning using GMA-*g*-PP as a compatibilizer in NBR/PP TPE.

In this article, a new compatibilized method was used to prepare TPE of NBR and PP with excellent mechanical properties by dynamic vulcanization. Amino-compound was used to react with GMA-*g*-PP first, because of lack of amino-terminated NBR in China, and then GMA-*g*-PP/ amino-compound was used as the compatibilizer. The effects of the curing systems, compatibilizer, PP type, kind and reprocessing on the mechanical properties of NBR/PP thermoplastic elastomers were investigated in detail.

EXPERIMENTAL

Raw Materials

A nitrile rubber (NBR) of N220S with AN content 40 wt % is the product of the JSR Co. in Japan. Two homo-polypropylenes, with melt flow rates of 1.8 and 7.2, were produced in the Shanghai Petrochemical Complex. GMA-*g*-PP (grafting degree 1.0%) was synthesized by ourselves. *Tert*-butyl phenolic resin is the product of the No. 1 reagent factory in Shanghai. Diethylene triamine (DETA), polyethylene polyamine (PEPA), hexamethyl tetramine (HMTA), stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), stearic acid (SA), calcium carbon-

ate, sulfur, dicumyl peroxide (DCP), and cyclohexene benzothiazole (CZ) were used as received.

Preparation of Compatibilizer

The reaction was carried out at 200°C and 80 rpm in a Haake Rheocord 90 batch mixer. After melting of the GMA-*g*-PP, desired amounts of a blend of amino-compound and calcium carbonate was added into the mixer. Five minutes later, 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 to be used as a compatibilizer in the following experiments. The basic formulation was GMA-*g*-PP 100, CaCO_3 10, DETA 10, unless otherwise specified.

Preparation of NBR/PP TPE

The preparation of NBR/PP thermoplastic elastomer was performed at 200°C and 80 rpm in a Haake Rheocord 90 batch mixer. Two minutes after melting of the PP/compatibilizer blend in the mixer NBR was added. Five minutes later, a blend of curative/calcium carbonate (1 : 1) then the curing coagent were added, and the mixing continuing. The mixing was continued until 5 min after the maximum in the mixing torque (due to curing) had occurred. The composition was removed from the mixer then sheeted by passing the hot mass through a hot twin-roll mill (180°C). The sheet was then compression molded in a press at 200°C, then cold pressed to give samples for testing. The basic formulation was NBR 50, PP 45, compatibilizer (mentioned above) 6, SA 1 phr, SnCl_2 0.5 phr unless otherwise specified.

Measurement

The tensile properties and tear strength of NBR/PP TPE were measured according to the Chinese Standard GB527-83 equivalent to ASTM

Table I Effect of Curatives on the Properties of NBR/PP TPE

Curatives	<i>Tert</i> -Butyl Phenolic-Resin	Sulfur	Dicumyl Peroxide (DCP)
Tensile strength (MPa)	14.84	13.65	11.60
Elongation at break (%)	436	144	99
Tension set at break (%)	172	40	24

Formulation: NBR 50, PP 45, Compatibilizer 6, SA 1 phr, Curative: (1) *tert*-butyl phenolic resin 4 phr, SnCl_2 0.5 phr; (2) Sulfur 1.5 phr, ZnO 5 phr, CZ 1.0 phr, (3) DCP 1 phr.

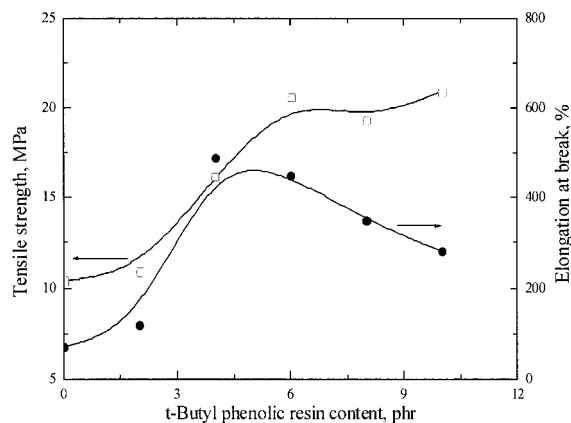


Figure 1 Effect of *tert*-butyl phenolic resin content on the properties of NBR/PP TPE.

D638M. Tension set at break was recorded 3 min after break. Shore A hardness was recorded 5 s after the presser foot contacted the sample. The apparent viscosity of TPE was measured with a capillary rheometer at 200°C. The length/diameter ratio (L/D) of the capillary was 40. For the viscosity and shear rate data, Rabinowitsch corrections were applied.

RESULTS AND DISCUSSION

Effect of Curatives

NBR can be vulcanized by different curatives such as sulfur, phenolic resin, and peroxide. Table I listed the mechanical properties of NBR/PP TPE cured with sulfur, *tert*-butyl phenolic resin, or dicumyl peroxide (DCP), respectively. It can be seen that PP/NBR TPE cured with *tert*-butyl phenolic resin has higher tensile strength and elongation at break than those with sulfur or DCP. Therefore, *tert*-butyl phenolic resin was chosen as the curative in subsequent experiments.

The effect of *tert*-butyl phenolic resin content on the properties of NBR/PP TPE is shown in Figure 1. The tensile strength increases rapidly with increasing *tert*-butyl phenolic resin content

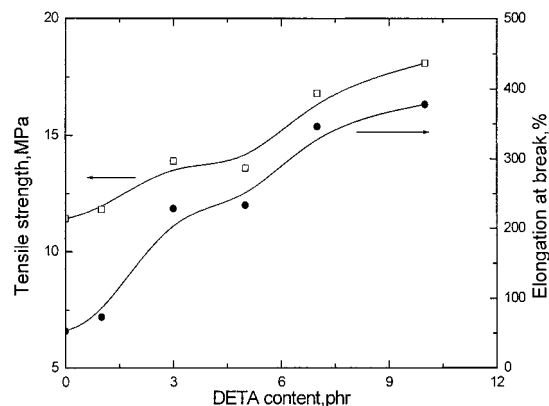


Figure 2 Effect of DETA content on the properties of NBR/PP TPE. Formulation: NBR 50, PP 45, Compatibilizer (GMA-*g*-PP: 100, CaCO₃: 10, DETA: X) 6, SA 1 phr, *tert*-butyl phenolic resin 4 phr.

and reached a high level of 20.6 MPa at a *tert*-butyl phenolic resin content of 6 phr. Meanwhile, the elongation at break goes through a maximum value of 490 at a *tert*-butyl phenolic resin content of 4 phr. The crosslinking degree of rubber phase increases with increasing *tert*-butyl phenolic resin content, which results in the increase of tensile strength. However, overrunning high crosslinking will impair the elongation at break. Therefore, the suitable *tert*-butyl phenolic resin content is 4–6 phr.

Effect of Compatibilizer

In this study, the amino-compound was first reacted with GMA-*g*-PP and the GMA-*g*-PP/amino-compound was used as the compatibilizer. Different amino-compounds were used, and their effects on mechanical properties of NBR/PP TPE are compared in Table II. It can be seen that DETA has the best effect. The effect of DETA content on properties of NBR/PP TPE is shown in Figure 2. The results show that NBR/PP TPE has low tensile strength and elongation at break when only using GMA-*g*-PP as the compatibilizer. Adding DETA increases the mechanical properties of

Table II Effect of Amino-Compound on the Properties of NBR/PP TPE

Amino-Compound	DETA	HMTA	PEPA
Hardness (shore A)	98	97	97
Tensile strength (MPa)	18.1	11.7	17.6
Elongation at break (%)	378	237	360

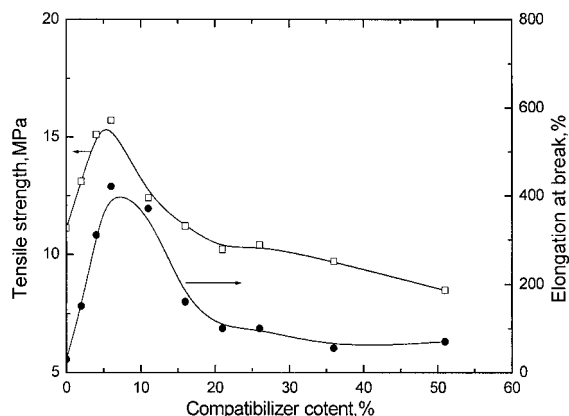


Figure 3 Effect of compatibilizer content on the properties of NBR/PP TPE.

NBR/PP TPE, and the properties increase greatly with increasing DETA content. For the NBR/PP TPE using 10 phr DETA, tensile strength increases about 70% and elongation at break increases 600% over that of TPE using no DETA. This may be due to the fact that GMA cannot react with NBR, and so there is no compatibilizing effect when only GMA-*g*-PP is used as the compatibilizer. When GMA-*g*-PP is used to react with DETA, which is then used as the compatibilizer, the unreacted amine groups may participate in the latter curing reaction initiated by *tert*-butyl phenolic resin.

Figure 3 shows the effect of GMA-*g*-PP/DETA compatibilizer content on mechanical properties. The tensile strength and elongation at break both go through a maximum value at a compatibilizer content of 6 phr. The reason for this may be that GMA-*g*-PP has poor mechanical properties, and too much GMA-*g*-PP will injure the properties of the NBR/PP TPE.

Effect of PP Content

The rubber/plastic proportion affects the properties of blends significantly. As shown in Table III,

tensile properties, hardness, and tension set at break of the NBR/PP TPE increase with increasing PP content. For the rubber/PP ratio of 80/20, the tensile strength was 13.3 MPa and the elongation at break was 310%, while the hardness was only 86, indicating the NBR/PP TPE at a ratio 80/20 rubber/plastic is an elastomer with excellent mechanical properties.

Effect of Melt Flow Rate of PP

Table IV shows the relationship of melt flow rate of PP on properties of the NBR/PP TPE. The higher the melt flow rate, the lower molecular weight of the PP. It can be seen that the tensile strength and elongation at break of the NBR/PP TPE increase with increasing the PP molecular weight. This is due to the PP being the continuous phase in TPE prepared by dynamic vulcanization, and the mechanical properties are decided by the continuous phase.

Effect of Reprocessing

An important advantage of TPEs over 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 the TPE. To illustrate this reprocessing ability of the NBR/PP TPE, the TPE was reprocessed five times by compression 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 were almost unchanged after reprocessing, and the apparent viscosity of the TPE increased only a little after reprocessing. This indicates that the NBR/PP TPE has good reprocessing ability.

Table III Effect of PP content on the Properties of NBR/PP TPE

PP content	50/50	60/40	70/30	80/20
Stress at 100% strain (MPa)	12.28	9.83	8.14	6.54
Tensile strength (Mpa)	15.99	14.98	14.00	13.30
Elongation at break (%)	480	380	340	310
Hardness (shore A)	97	96	92	86
Tension set at break (%)	228	108	60	40

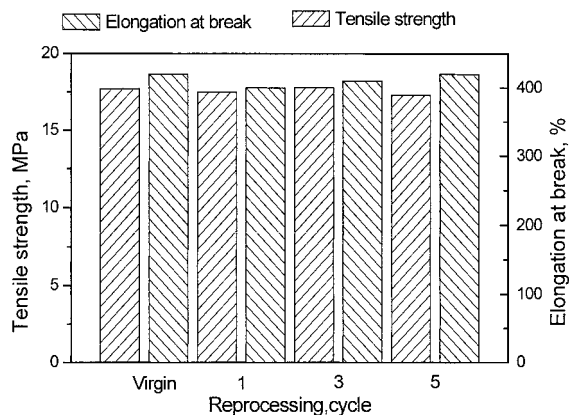
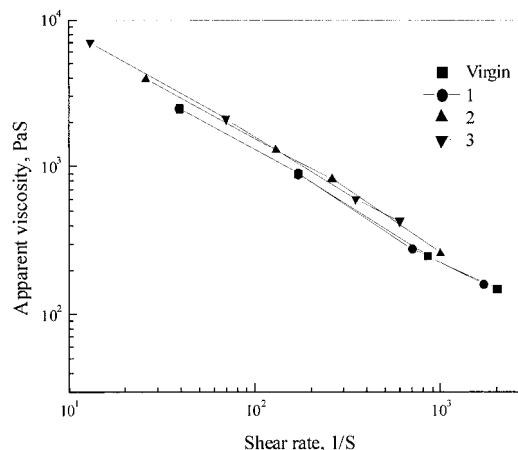
Formulation: NBR+PP 100, Compatibilizer 6, SA 1 phr, *tert*-butyl phenolic resin 4 phr, SnCl₂ 0.5 phr.

Table IV Effect of PP Molecular Weight on the Properties of NBR/PP TPE

MFR of PP (g/10 min)	7.2	1.8
Stress at 100% strain (MPa)	12.80	12.53
Tensile strength (MPa)	13.01	15.75
Elongation at break (%)	280	427
Hardness (shore A)	97	97
Tension set at break (%)	156	160

CONCLUSIONS

A thermoplastic elastomer (TPE) composition of nitrile rubber (NBR) and polypropylene (PP) with excellent mechanical properties was prepared by dynamic vulcanization using a glycidyl methacrylate (GMA) grafted PP/amino-compound reaction product as the compatibilizer. The addition of amino-compound in the compatibilizer can significantly increase the mechanical properties of NBR/PP thermoplastic elastomer. Compared with other amino-compounds, diethylenetriamine (DETA) has the best effect. PP with higher molecular weight is more suitable for preparing NBR/PP thermoplastic elastomer with high ten-

**Figure 4** Retention of tensile properties of reprocessed NBR/PP TPE.**Figure 5** Rheological properties with reprocessed NBR/PP TPE.

sile strength and high elongation at break. The NBR/PP TPE has good reprocessing ability.

REFERENCES

- Gessler, M. U.S. Pat. 3,037,954 (1962).
- Fisher, K. U.S. Pat. 3,758,643 (1973).
- Coran, A. Y.; Patel, R. P. *Rubber Chem Technol* 1980, 53, 141.
- Tang, T.; Hu, C. P.; Yin, S. K., et al. *Adv Polym Blends Alloys Technol* 1993, 4, 1.
- Zhang, X.; Zhang, X.; Peng, Z.; et al. *J Appl Polym Sci* 2000, 77, 2641.
- Coran, A. Y.; Patel, R. *Rubber Chem Technol* 1983, 56, 1045.
- Coran, A. Y.; Patel, R. U.S. Pat. 4,355,139 (1982).
- Coran, A. Y.; Patel, R. U.S. Pat. 4,409,365 (1983).
- George, S.; Joseph, R.; Thomas, S.; Varughese, K. T. *Polymer* 1995, 36, 4405.
- George, S.; Neelakautan, N. R.; Varughese, K. T.; Thomas, S. J. *J Polym Sci B Polym Phys* 1997, 25, 2309.
- George, S.; Kamamurthy, K.; Anamd, J. S.; Groeninecx, G; Varughese, K. T.; Thomas, S. J. *Polymer* 1999, 40, 4325.
- George, S.; Varughese, K. T.; Thomas, S. *Polymer* 2000, 41, 5485.