

Compounding Studies of a Fluoroelastomer

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ABSTRACT

Compounding studies of a fluoroelastomer grade (Viton GF) has been carried out. The effect of peroxide cross-linking system is compared with hexamethylene-*N,N'*-bis(tert-butyl peroxy carbamate) (HBTBP). HBTBP in fluoroelastomer produced a comparative cure response as the conventional peroxide system. Whereas, co-agents are necessary to bring about cure in peroxide systems, it was found that HBTBP does not need co-agents to cure this fluoroelastomer grade. Also, only calcium oxide and magnesium oxide are compatible with HBTBP cure.

Key Words:

fluoroelastomer;
cure/vulcanization;
compounding;
HBTBP.

INTRODUCTION

Fluoroelastomers are highly fluorinated polymers and they are well-known for their outstanding heat and fluid resistance. Their stability has been attributed [1, 2] to the strength of the carbon-fluorine bond compared to that of the carbon-carbon

bond, to steric hindrance and to strong van der Waals forces between hydrogen and fluorine atoms present in the macromolecules. It is because of their properties that fluoroelastomers are used in application fields such as automotive, aerospace, mili-

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tary, chemical, oil-well and other industries where the harsh environment and increasing severity of operating conditions necessitate the use of a stable elastomer. The standard compounding practice of fluoroelastomers has been documented [2]. Usually, most fluoroelastomer compounds have a typical formulation shown below:

Fluoroelastomer	100
Metal oxide	3-15
Filler	10-30
Processing aid	0.5-2.0
Curing agent	0.5-4.0

The metal oxide in the formulation is used as acid acceptor in curing reactions while fillers are used to reduce cost, to facilitate processing by reducing nerve of the uncured stock and to adjust hardness and modulus. Processing aids used to compound fluoroelastomers are usually proprietary compounds. When processing aids are used in a compound, one or more vulcanizate properties may be compromised. As in all other rubber compounds, curing agents are always added to fluoroelastomer compounds. We have previously reported the use of HBTBP as cross-linking agent in fluoroelastomer and some other elastomers [3 - 5]. It was found that a relatively good cure was obtained when HBTBP was used as a cross-linking agent in fluoroelastomers and consequently, further compounding studies was carried out.

The aims of this work are: (i) to compare the use of HBTBP and peroxides as cross-linking agents in fluoroelastomers; (ii) the effect of triallylisocyanurate co-agent on properties of HBTBP-cured vulcanizates; and (iii) to find the effect of using different metal oxides on properties of HBTBP-cured fluoroelastomers.

EXPERIMENTAL

Materials

The Viton GF brand of fluoroelastomers and triallylisocyanurate (Diak No 7) were obtained from du Pont (UK) Limited. Calcium hydroxide and calcium oxide were obtained from John & E. Sturge Limited, UK. Luperco 101 - XL (2,5-dimethyl-2,5-bis[tert-butyl peroxy] hexane), 45% active ingredient on inert carrier was obtained from K and K Greef Chemicals Limited, UK. Other compounding ingredients were standard

materials used in rubber formulations and they were used in compounding as received. HBTBP was prepared as described in the literature [6].

Compounding and Testing

The fluoroelastomer and compounding ingredients were mixed on a two-roll mill of 850 mL capacity at 40 C. A modification was the pre-blending of all compounding ingredients before addition on the mill. The compound was refined on tight mill, 24 h after mixing to enhance dispersion.

Mooney scorch was determined according to the principles laid down in BS 1673 Part 3, 1969, while the cure response of the compounds was determined with the aid of a Monsanto oscillating disc rheometer TM 100 using the test procedure specified in BS 1673; Part 10, Method B, 1977.

The mixed compound was press-cured at 170 C for 15 min and the resulting vulcanizates were post-cured for 24 h in an air-oven at 250 C (A two-step cure is the practice with fluoroelastomers). The tensile stress-strain properties of the resulting vulcanizates were determined according to BS 903; Part A2, 1971, using Type 2, dumb-bell specimens, and compression set was determined as described in BS 903 Part A6, 1969.

RESULTS AND DISCUSSION

Comparison of HBTBP and Peroxide Cure in Fluoroelastomers

The oscillating disc rheometer (ODR) traces for the HBTBP compound and the control compound are shown in Figure 1; the figure demonstrates that the fluoroelastomers could be formulated with HBTBP to obtain about the same level of cure with the control compound. A particular problem with the use of HBTBP is the evolution of carbon dioxide during cure. Although this problem was overcome by the inclusion of calcium hydroxide in the formulation, it was more pronounced at increased levels of HBTBP.

Vulcanizates of the compound containing HBTBP at 5 phr level (to reduce CO₂ evolution) and that of the control compound (peroxide) were prepared. The physical properties, shown in Table 1, were obtained for samples in both the post-cured and non-post-cured states. The results clearly demonstrate that fluoroelas-

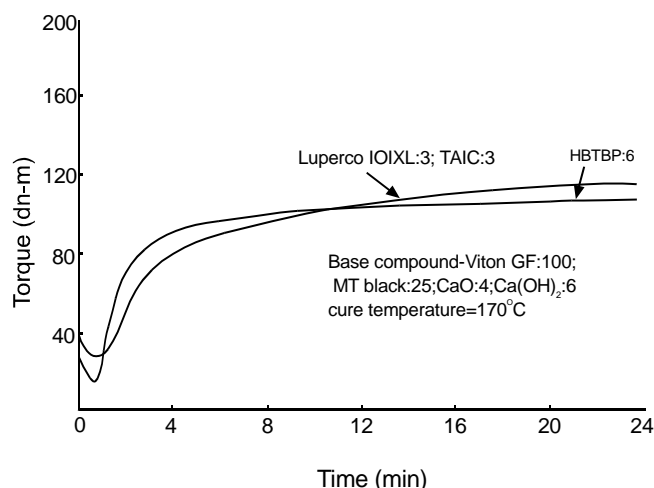


Figure 1. Comparison of cure traces obtained using HBTBP and peroxide cures in Viton GF respectively.

Fluoroelastomer compounds cured with HBTBP respond to post-curing operation as with other established cross linking systems. The mechanism of cross-linking of the fluoroelastomers with HBTBP has been discussed in a previous work [4] and it is not considered here.

Effect of Co-agent

According to literature [1], the fluoroelastomer is cured only by a combination of peroxides and co-agents; the co-agent recommended being triallylisocyanurate (Diak No 7). Hence it was investigated whether triallylisocyanurate is compatible with HBTBP and the effect of increasing co-agent concentration on vulcanizate properties.

The cure traces obtained for the various concentra-

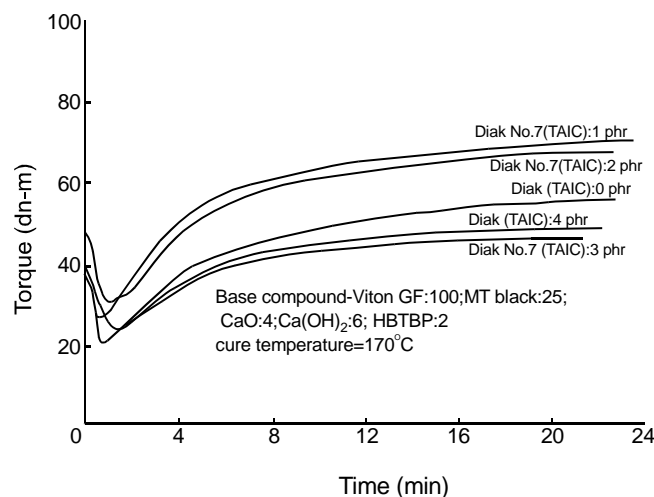


Figure 2. Effect of co-agent on HBTBP-cure of Viton GF.

tions of co-agent are shown in Figure 2, while the properties of the corresponding vulcanizates are shown in

Table 1. Physical properties of Viton GF cured by HBTBP and peroxide.

Compounding agents	HBTBP	Peroxide
Viton GF	100.0	100.0
MT Black (990)	25.0	25.0
CaO	4.0	4.0
Ca(OH) ₂	6.0	6.0
HBTBP	5.0	
Luperco 101-XL	-	3.0
Co-agent (Diak No 7)	-	3.0
Mooney scorch at 120°C (min)	5.5	>40
Cure conditions	15 min at 170 °C	15 min at 170 °C

Original vulcanizate properties (no post-curing).

Properties	HBTBP	PEROXIDE
Tensile strength (MPa)	11.32	8.42
Elongation-at-break (%)	250	550
100% Modulus (MPa)	3.54	3.42
Compression set, 70 h at 250°C (25% strain)	Sample cracked or contained voids	—
Hardness IRHD	—	—

Vulcanizate properties (air-oven post-cured at 250°C for 24 h).

Properties	HBTBP	PEROXIDE
Tensile strength (MPa)	13.73	18.47
Elongation-at-break (%)	150	200
100% Modulus (MPa)	9.59	11.08
Compression set, 70 h at 250°C (25% strain)	Sample cracked or contained voids	68
Hardness IRHD	—	58

Table 2. Effect of triallylisocyanurate (TAIC) on the properties of HBTBP-cured Viton GF compound.

Compounding agents	Control	C1	C2	C3	C4
Viton GF	100.0	100.0	100.0	100.0	100.0
MT Black (N(990)	25.0	25.0	25.0	25.0	25.0
CaO	4.0	4.0	4.0	4.0	4.0
Ca(OH) ₂	6.0	6.0	6.0	6.0	6.0
HBTBP	2.0	2.0	2.0	2.0	2.0
Diak No 7 (TAIC)	-	1.0	2.0	3.0	4.0
Mooney scorch at 120°C (min)	6.5	2.0	2.0	2.0	2.0
Cure conditions (min/°C)	15/170	15/170	15/170	15/170	15/170

Original vulcanizate properties (no post-curing).

Properties	Control	C1	C2	C3	C4
Tensile strength (MPa)	11.14	10.68	10.71	10.39	10.25
Elongation-at-break (%)	400	325	350	375	350
100% Modulus (MPa)	3.8	4.13	3.81	3.87	3.95
Compression set (70 h at 250°C, 25% strain)	**	**	**	**	**
Hardness IRHD	51	52	54	54	54

Vulcanizate properties (air-oven post-cured at 250°C for 24 h)

Properties	Control	C1	C2	C3	C4
Tensile strength (Mpa)	14.28	16.03	14.66	15.75	15.32
Elongation-at-break (%)	250	200	200	200	200
100% Modulus (MPa)	5.71	10.33	7.69	8.63	9.07
Compression set (70 h at 250°C, 25% strain)	98	86	88	89	87
Hardness IRHD	54	57	58	56	59

(**) Samples were permanently deformed

Table 2. The use of co-agent decreased the safe processing times as shown by the Mooney scorch values. The ODR cure traces do not seem to follow any definite pattern. It is, however, noteworthy that the use of 1 phr and 2 phr of co-agent with HBTBP, respectively, gave higher ODR torques than the compound without co-agent.

Explanation for the nature of the ODR traces is unknown but it was satisfying that the use of co-agent led to an overall improvement in properties; the improvement to compression set resistance was significant while the effects on other properties were rather

insignificant. In the light of available results, it could be said that HBTBP, whilst being compatible with triallylisocyanurate co-agent in fluoroelastomer, it does not necessarily require a co-agent to cure effectively.

Effect of Metal Oxides

Some formulations (Table 3) were prepared to find out whether other metal oxides apart from calcium oxide could be used in HBTBP curing of fluoroelastomers. The metal oxides investigated were magnesium oxide and lead oxide. It must be stressed, however, that whatever oxide is used, a material that would absorb the car-

Table 3. Effect of metal oxides on viton GF vulcanizate properties.

Compounding agents	Calcium oxide	Magnesium oxide
Viton GF	100.0	100.0
MT Black (N990)	25.0	25.0
CaO	4.0	—
MgO	—	3.0
Ca(OH) ₂	6.0	6.0
HBTBP	3.0	3.0
Cure conditions (min/S/°C)	15/170	15/170

Original Vulcanizate Properties (No Postcuring).

Properties	Calcium oxide	Magnesium oxide
Tensile strength (MPa)	11.24	12.84
Elongation-at-break (%)	300	325
100% Modulus (MPa)	3.2	3.55
Hardness IRHD	51	51

Vulcanizate properties (air-oven post-cured at 250°C for 24 h).

Properties	Calcium oxide	Magnesium oxide
Tensile Strength (Mpa)	11.24	12.84
Elongation-at-break (%)	300	325
100% Modulus (MPa)	3.2	3.55
Hardness IRHD	51	51

bon dioxide evolved during vulcanization is always an essential part of the formulation-hence the inclusion of calcium hydroxide in the formulations. The cure traces for compounds containing magnesium oxide and calcium oxide were almost the same and so they were not included. The physical properties of the vulcanizates containing magnesium oxide are compared with that containing calcium oxide in Table 3; this shows that whether calcium oxide or magnesium oxide is used, there is little difference in the properties of vulcanizates produced. On the other hand, the use of lead oxide in HBTBP curing of fluoroelastomer gave a formulation

with a low state of cure and the vulcanizate produced was porous despite the inclusion of calcium hydroxide. This would seem to indicate that the use of (lead oxide) litharge interferes with cure in HBTBP systems. So far, calcium oxide and magnesium oxide are the metal oxides found to be compatible with HBTBP curing systems.

CONCLUSION

A general compounding study of fluoroelastomer has been undertaken. The vulcanizates obtained from HBTBP-cure of the fluoroelastomer are not as good as those of conventional peroxide vulcanizates. It was further established that an HBTBP-cure does not necessarily require a co-agent to cure effectively. Also, magnesium and calcium oxides were found to be compatible with the HBTBP curing system while lead oxide is unsuitable.

REFERENCES

1. Apotheker D., Finlay J.B., Krusic P.J., and Logothetis A.L., Curing of fluoroelastomers by peroxides, *Rubb. Chem. Technol.*, **55**, 1004-1018 (1982).
2. Arnold R.G., Barney A.L., and Thompson D.C., Fluoroelastomers, *Rubb. Chem. Technol.*, **46**, 619-652 (1973).
3. Ogunniyi D.S. and Hepburn C., Hexamethylene-*N,N'*-bis(tert-butyl peroxy carbamate as a curing agent for fluoroelastomers, *Plast. Rubb. Process. Appl.*, **6**, 3-9 (1986).
4. Ogunniyi D.S., A novel system for crosslinking fluoroelastomers, *Rubb. Chem. Technol.*, **61**, 735-746 (1988).
5. Ogunniyi D.S. and Hepburn C., Hexamethylene-*N,N'*-bis(tert-butyl peroxy carbamate as a crosslinking agent in some elastomers, *Iran. J. Polym. Sci. Tech.*, **3**, 48-59 (1994).
6. Pedersen C.J., Preparation and properties of esters of *N*-substituted peroxy carbamic acids, *J. Org. Chem.*, **23**, 252-255 (1958).