The effect of curing on sorption and diffusion of a brake fluid in EPDM elastomer

*Tahereh Darestani Farahani *, Gholam Reza Bakhshandeh*

Rubber Group, Processing Faculty, Iran Polymer and Petrochemical Institute (IPPI),
P.O. Box 14965/115, Tehran, Iran; Fax (+9821) 4580054; t.darestani@ippi.ac.ir,
g.r.bakhshandeh@ippi.ac.ir

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Abstract: The effect of a poly(ether glycol) brake fluid on cured EPDM (ethylene-propylene-diene monomer) elastomer based on 5-ethylidene-2-norborene has been studied. Different amounts of dicumyl peroxide (DCP) curing agent were used and the effect of ageing in a brake fluid (at 100°C for 70 h) on technical properties of EPDM have been investigated. By increasing the amount of DCP, significant changes were not observed. Tensile strength and modulus increased but elongation at break and abrasion loss decreased due to oxidative degradation and crosslinking. Hardness was constant due to the replacement of plasticizer with brake oil.

Introduction

EPR (ethylene-propylene rubber) is a saturated synthetic elastomer. It is inherently resistant to degradation by heat, light, oxygen and in particular ozone [1]. EPDM elastomers (ethylene-propylene-diene monomer), which contain pendent unsaturation, like ENB (5-ethylidene-2-norborene), are only slightly less stable to ageing than EPR [1,2]. EPDM is used in a wide range of applications especially as an outdoor electrical insulator [3], and in a variety of automotive applications (41% of the worldwide uses) [4-6], e.g., brake systems, O-rings and gaskets [7,8].

Brake (hydraulic) fluid is composed of a lubricant (e.g., propylene glycol), a solvent blend (mixture of glycol ethers) and additives for corrosion resistance [9]. We have undertaken an investigation on the effect of poly(ether glycol) brake fluid, commercially known as DOT3, toward an EPDM elastomer based on ENB.

The investigations carried out over the past several years showed that the molecular transport of organic liquids depends on (1) the density of chain entanglements and chain ends, (2) crosslink density, (3) compatibility of both polymer and liquid, and (4) the type and the amount of filler in addition to viscosity of the penetrating liquid and the functionality of crosslinks [8]. Since crosslink density is crucial to the transport properties of EPDM elastomer, different amounts of dicumyl peroxide (DCP) curing

agent were used with other compounding ingredients that EPDM manufacturing suppliers utilize for brake parts.

Ageing of rubber vulcanizates considerably changes the network structure, which in turn controls the technical properties. These changes depend on both temperature and time of ageing [10]. Therefore, the effect of ageing in a brake fluid on technical properties of EPDM vulcanizates with different crosslink density has been studied.

Experimental part

Materials

Details of used materials and compounding formulations are given in Tabs. 1 and 2, respectively.

Tab. 1. Materials

	Material	Traditional name	Supplier
EPDM	55.5% ethylene content ML(1+4) at 125°C = 91	Vistalon 7500	Exxon (Korea)
DCP	dicumyl peroxide (40%)	-	Taiwan oil product corp.
oil	paraffinic	Behran 840	Behran Oil Company (Iran)
N-330	carbon black	-	Carbone Ahvaz (Iran)
IPPD	antioxidant	NA-4010	Bayer (Germany)
ZnO	zinc oxide	-	Iran
st. acid	stearic acid	-	Malaysia

Tab. 2. Compounding formulation (expressed in parts per hundred parts of resin, phr)

Ingredient	A	B	C	D
EPDM	100	100	100	100
N-330	70	70	70	70
oil	10	10	10	10
IPPD	1.5	1.5	1.5	1.5
ZnO	5	5	5	5
st. acid	2	2	2	2
DCP	2	4	6	8

Mixing

EPDM rubber, filler, oil and antioxidant (IPPD) were mixed in a laboratory Banbury machine (Farrell) for 12 min and DCP was added to master batch using a laboratory two-roll mill (Polymix).

Curing

The cure characteristics (t_5 , scorch time, and t_{95} , cure time) were determined using a Zwick rheometer model ODR. Then the compounds were compression molded at 170°C based on the respective t_{95} value in a hydraulic press.

Measurement of mechanical properties

Tensile properties were measured following ASTM D 638 using a MTS tensometer at 500 mm/min crosshead speed. Hardness (shore A), resilience and abrasion loss were determined using Zwick testers according to ASTM D 2240, D 1054 and D 5963, respectively. A four-digit laboratory balance (Precisa, Switzerland) was used in abrasion tests.

Swelling studies

Oil resistance of vulcanizates was measured at 100°C for 70 h. Brake oil Lockheed, super 105, DOT3 (England) was used. EPDM samples were cut into uniform rectangular pieces of size 2 x 20 x 40 mm. Dry weights of the cut samples were determined before immersion in oil and at specified time intervals when the samples were taken out, immersed in ethyl alcohol, then dried between two filter papers and weighed using an analytical balance. Samples were immediately placed back into the test bottle and returned to the oven.

We also examined the effect of ageing on mechanical properties of the samples. It should be noted that the samples were post-cured at 100°C for 24 h before swelling and mechanical tests.

Ageing studies

According to previous studies [11], tensile, abrasion and hardness samples were immersed in brake oil at 100°C for 70 h. Changes of the above properties of specimens after oil immersion were used to determine oil resistance, as shown in Eq. (1). The relative property (P_{rel}) including tensile strength, modulus, elongation at break, hardness and abrasion, was calculated from the ratio of property after (P_{after}) to before (P_{before}) oil immersion.

$$P_{rel} = \frac{P_{after}}{P_{before}} \quad (1)$$

It should be noted that the samples were post-cured at 100°C for 24 h before swelling. For mechanical and ageing tests at least three samples were used and the results of all samples were analyzed for error and average results were reported.

Results and discussion

Sorption results

Sorption results are expressed in terms of mass increase per 100 g of EPDM rubber (Q_t , sorption vs. time). Plots of Q_t in Fig. 1 show that formulations reached the maximum sorption in the first 2 h. Then they showed a sudden decrease with time, possibly creating the additional free volume necessary for the diffusion of molecules

of the brake fluid so that the advancing boundary travels faster than the rate of relaxation of EPDM chain segments. However, this pattern levelled off and reached saturation in which no more leaching was observed.

Fig. 1. Sorption versus time (Q_t) at 100°C for 70 h in the brake fluid: (A) 2 phr DCP, (B) 4 phr DCP, (C) 6 phr DCP and (D) 8 phr DCP

The decrease in Q_t values over an extended period of time after reaching maximum sorption is striking. The same phenomenon has been documented in the literature [7] and is attributed to the loss of low-molar-mass indigenous compounds in the presence of aggressive solvents. In addition, this study showed that the leaching out of the indigenous additives occurs for formulations embedded with paraffin oil and formulations without paraffin oil exhibit sigmoid trends.

Even though there has been no systematic study to check out the immiscibility of paraffin oil and the brake fluid, it is likely that when the latter diffuses into the EPDM elastomer network, it might replace the paraffin oil and act as a plasticizer without any change in hardness [8]; our observations support this idea.

Increasing the DCP amount, very significant changes were not observed: the first maximum swelling increased and the saturated leaching decreased. It should be noted that difference is less than 1%. Previous results indicate that the degree of swelling of rubber vulcanizates decreases with increasing number of crosslinks (crosslink density CLD) [12] and it is predicted that increasing DCP causes an increasing number of crosslinks. The changes of mechanical properties supported this idea (see next section).

According to the above idea – diffusion of brake oil in the EPDM compound – the final leaching should be decreased with increasing DCP amount, but our results showed a slight increase instead. Tab. 3 shows the final swelling and the amount of leached oil calculated. We supposed that all mass loss was caused by leaching of paraffinic oil.

It can also be seen that the fraction of leached oil increased with increasing DCP amount while the amount of oil in the compound decreased. It seems that increasing DCP amount and degradation (i.e., breakdown of peroxide bonds) make the EPDM

compound somewhat more polar, thereby increasing the diffusion of polar liquid such as brake fluid into compound and leaching of indigenous paraffin. This is in agreement with the previous works [8], which showed that increasing the amount of double bonds in the rubber, such as increasing the ENB content of EPDM rubber, tends to increase the diffusivity for octadecane in the unsaturated rubber and the hydrogenated polymers.

Tab. 3. Oil fraction in compounds and leaching data

	Formulation			
	A	B	C	D
Oil in compound (phr)	10	10	10	10
Oil in compound (wt.-%)	5.32	5.20	5.14	5.10
Final swelling (wt.-%)	-3.2	-3.4	-3.6	-3.8
Leached oil (wt.-%)	61.2	65.2	66.2	76.5

Tab. 4. The properties and test results for each sample (U = unaged, A = aged)

	Formulation							
	A		B		C		D	
	U	A	U	A	U	A	U	A
Tensile strength in MPa	4	5.6	15	18.4	20.3	21.6	18.2	22.6
Modulus 100% in MPa	1.4	1.7	1.6	2.3	2.1	3.3	1.9	3.8
Modulus 300% in MPa	2.2	3.7	3.6	7.6	6	13.8	6	18.3
Elongation at break in %	870	464	956	561	660	408	580	338
Hardness (Shore A)	60	62.8	40	64.7	63.8	68.8	69	68.4
Abrasion loss in wt.-%	11.27	8.63	7.03	6.23	5.7	5.37	4.9	5.4
Final swelling in wt.-%	-	-3.2	-	-3.4	-	-3.6	-	-3.9

Mechanical properties

Tab. 4 shows the properties of the samples before and after 70 h ageing in brake oil at 100°C. The results illustrated in Figs. 2 and 3 show gradually increasing values of tensile strength and modulus due to DCP addition. However, the values of tensile strength began to decrease at DCP fractions higher than 6 phr.

The increases in the tensile strength and modulus could be attributed to the rising number of crosslinks, by further addition of DCP curing agent to the EPDM rubber formulation. On the other hand, the observed decrease in tensile strength at higher addition could be due to over-crosslinking. Over-crosslinking occurs when M_c (i.e., the chain length between crosslinks) is very low. As a result, elongation at break decreases due to the low motion of crosslinked chains. Thus, the sample breaks before it can reach its maximum attainable tensile strength. In an aged sample, this phenomenon cannot be observed due to an increasing modulus that causes higher tensile strength at lower elongation at break than for the unaged sample.

Relative increases in tensile strength and modulus were observed after ageing in brake fluid at 100°C (Figs. 2 and 3, respectively), which is due to oxidative degra-

ation and increasing stiffness. However, some studies showed that crosslinking reactions can occur in EPDM compounds on the same time scale as oxidation because both oxidation and crosslinking reactions involve radical processes [13,14].

Fig. 2. The effect of DCP amount and ageing on tensile strength

Fig. 3. Effect of DCP amount and ageing on modulus

In the case of elongation at break (Fig. 4), ageing causes reduction of elongation. It is to emphasize that the trends in modulus, tensile strength and elongation indicate degradation in their own respect. The same results have been reported in ref. [15]. Dunn [16] also reported the same phenomenon in NBR due to oxidation following radical attack on allylic hydrogen.

The results shown in Fig. 4 also show a gradual decrease in the values of elongation at break in both unaged and aged samples due to the addition of DCP. But the value of elongation at break at 2 phr DCP is less than of compound B (4 phr DCP). The reason for this reduction is the rising number of crosslinks by further increasing the

DCP fraction in EPDM compound and the first observed decrease at low DCP amount could be due to under-crosslinking.

Fig. 4. Effect of DCP amount and ageing on elongation at break

Figs. 5 and 6 show the effect of DCP amount and ageing of EPDM on abrasion loss and hardness, respectively. It can be seen that both abrasion resistance and hardness increase with increasing DCP amount due to a rising crosslink density (CLD). Low abrasion resistance (i.e., high abrasion loss) and hardness in compound A (2 phr DCP) could be attributed to under-crosslinking.

Ageing causes a relative increase in abrasion resistance and weight loss of aged samples is less than that of unaged samples. This observation can also be attributed to the oxidative degradation and increasing stiffness of aged samples, or to the crosslinking reaction during ageing.

Fig. 5. Effect of DCP amount and ageing on abrasion loss

Fig. 6. Effect of DCP amount and ageing on hardness

In the case of hardness, after ageing in the brake fluid, no significant change was observed in sample hardness. It is likely that when the brake fluid diffuses into the EPDM elastomer network, it might replace the paraffinic oil and act as a plasticizer without any change of hardness. The same phenomenon has been reported in the literature [7].

In sample D, it seems that more than optimum amount of peroxide causes radical formation and degradation during ageing due to EPDM chain breakdown. This phenomenon increases abrasion loss and hardness of sample D with ageing.

Fig. 7. Relative properties (properties after ageing/properties before ageing)

Fig. 7 shows the relative properties (properties after ageing/properties before ageing). It can be seen that hardness and elongation at break changes are the same for all samples. Elongation at break of all samples after ageing is approximately half

of the value before ageing (i.e., relative elongation at break is 0.5 - 0.7) and hardness of all samples does not change during ageing test.

Tensile strength and modulus changes increase with increasing DCP amounts. It is likely that in ageing conditions both the oxidative degradation and crosslinking reaction, which are due to the presence of radicals, are raised by further addition of DCP curing agent in these formulations.

Relative abrasion loss increases (i.e., there is a decrease in abrasion resistance) by addition of DCP in the compounds. Relative abrasion loss of samples containing less than 6 phr DCP is lower than 1, for 6 phr it is 1 and for 8 phr it is slightly more than 1. Therefore, abrasion resistance of samples containing less than 6 phr DCP increased by ageing and abrasion resistance of the 6 phr DCP sample doesn't change.

It seems that for low DCP contents, there is not enough free or active DCP for over-crosslinking or thermal degradation and oxidative degradation is the major mechanism of ageing but for high DCP content (6 - 8 phr) crosslinking and thermal degradation during ageing are more likely.

Conclusion

Our results show that the leaching out of indigenous additives occurs for EPDM formulations embedded with paraffin oil. By increasing the DCP amount, significant changes were not observed in maximum swelling (that occurs in the first 2 h) and saturated leaching.

After ageing, mechanical properties such as tensile strength, modulus and abrasion resistance decreased due to oxidative degradation and increasing stiffness. However the crosslinking reaction can occur on the same time scale as oxidation. Ageing causes a reduction of the elongation at break.

In addition, no significant change was observed in hardness after ageing in the brake fluid due to the replacement of paraffinic oil with brake fluid.

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