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난연제를 함유한 에틸렌-프로필렌-디엔-터모노머 고무컴파운드의 수명예측

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Lifetime Prediction of Flame Retardant-Filled Ethylene-Propylene-Diene-Termonomer Rubber Compounds

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초록: 여러 가지 난연제(Sb_2O_3, 브롬 및 염소계 난연제)를 함유하는 에틸렌-프로필렌-디엔-터모노머(EPDM) 고무컴파운드의 수명을 예측하였다. 각 고무 컴파운드에 대해 120, 135, 150, 165 ℃ 온도조건에서 열노화를 진행하고 노화전후의 인장특성을 조사하였다. 본 연구에서는 노화전 파단신장률이 50%로 감소되는 시간을 수명이라 정의하고 Dakin-Arrhenius 방정식을 이용하여 수명을 예측하였다. 미충전 EPDM과 Sb_2O_3을 함유한 EPDM의 경우 상온에서 100년에 가까운 수명이 예측되었다. 그러나 브롬계 난연제를 단독 혹은 Sb_2O_3와 혼용한 EPDM의 경우 미충전 EPDM 수명의 절반으로 감소하였다. 염소계 난연제를 단독 혹은 Sb_2O_3와 혼용한 EPDM의 경우 각각 90년과 82년으로 예측되었다.

Abstract: The lifetime of ethylene-propylene-diene-termonomer (EPDM) based rubber compounds with various flame retardants (FRs) including antimony trioxide (Sb_2O_3), halogenated (Br, Cl) materials and their combinations with Sb_2O_3 have been explored in this study. The tensile properties of the compounds have been evaluated before and after the thermal ageing over a range of temperatures, 120, 135, 150 and 165 ºC for different span of time. A 50% reduction in elongation at break (EB) due to thermal ageing is fixed as a failure criterion to predict the lifetime with the help of Dakin-Arrhenius equations. The predicted lifetime of the base EPDM and its Sb_2O_3-filled compounds shows almost 100 years at ambient temperature. However, the bromine containing flame retardant-filled EPDM as well as its combination with Sb_2O_3-filled EPDM compounds have reduced their lifetime to almost half of the lifetime of base EPDM. The predicted lifetime of EPDM compounds with chlorine containing FR and its combination with Sb_2O_3 shows around 90 years and 82 years, respectively.

Keywords: lifetime prediction, thermal aging, flame retardant, EPDM, tensile properties.

Introduction

Rubbers are one of the most versatile materials widely used in different applications. Rubbery materials are highly deformable by the application an external force in the form of even a small stress or strain. A vulcanized rubber material keeps a memory of its original unstressed state and will return to its initial state after removing the deformation force even if it is a quite large deformation. Rubbers exhibit good corrosion resistance, damping efficiency, non-conductivity towards heat and electricity as compared to metals. Owing to these unique characteristics of rubbers they find a prominent place in applications like tires, bridge bearing, engine mounts, and wire and cable insulations.[1-3]

Nowadays, much more attention is paid to improve the flame retardant properties of elastomers as it is an essential requirement

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for elastomers used in wire and cable insulation purposes. General method to improve flame retardant (FR) property of an elastomer is to add materials having flame retarding capability directly into the elastomer while compounding. The FRs can emit substances that displace the oxygen needed for a fire to burn; it can form a protective coating on the surface of flammable substrate, thereby limiting access to the fire to fuel sources, or it can do a combination of both.[4,5] Halogenated flame retardants such as chlorinated or brominated organo compounds are most effective and widely used flame retardants in plastics and elastomers. Owing to the toxicity and environmental issues raised by the halogenated flame retardants some halogen free flame retardants like Sb_2O_3 are promoted to use in elastomers and polymers. Generally Sb_2O_3 alone has no flame retarding capability and is often used as a synergistic combination with the organohalogen compounds. However, the sole use of Sb_2O_3 as flame retardants in polymers have also been reported.[6]

Ethylene-propylene-diene termonomer (EPDM) is one of the distinguished synthetic elastomers with excellent properties and is often used as an insulating sheath for cables particularly the cables for atomic power plants. To make EPDM as a promising elastomer for using as insulating material for wires and cables various flame retardants are added to the rubber while compounding. Several works have been performed on EPDM compound aimed to enhance their flammability behaviour.[7-9] Recently, the authors have also reported the effect of thermal ageing on the degradation mechanism of various FRs filled EPDM compounds.[10]

Unlike metals, the components made out of rubbers undergo several physical and chemical changes particularly when it is used for a very long time due to environmental ageing factors such as temperature and radiation. The physical or chemical changes include hardening, softening, cracking and surface tackiness etc. These physical changes of the rubber components weaken its functional performance, which ultimately leads to a premature removal of the component from service. For instance, rubbers are widely used for rubber engine mounts because of its damping efficiency. If the rubber mounts get hardened during service due to ageing it may lose its damping capability. Likewise, rubber materials are used as insulation materials for various types of cables such as cables used in sea water, cables in atomic power plants, computer systems etc. The service performance of these cables, particularly the cables in atomic power plants, cannot be or almost impossible to inspected frequently. If any degradation of such insulating materials due to, for instance, over voltage surges, external temperature raises, environmental stresses during operation leads to failure of the product before the anticipated time.[11] Therefore, lifetime prediction of rubber components is very essential to assure the safety as well as reliability particularly when it is used under stringent atmospheric conditions. The lifetime prediction studies of polymeric materials are mainly based on the changes in the materials properties after being exposed to accelerated thermal ageing. Failure times or degradation rates are determined at elevated temperatures and these data are used to extrapolate the materials performance at working or service conditions.[12-16]

Dakin proposed a theory describing the thermal deterioration of insulating materials in terms of Arrhenius chemical rate equation which is the widely used method for estimating the insulation lifetime.[17,18] The Dakin equation is

$$t_F = F(P_L)/K(T) \tag{1}$$

where P_L is the value of the physical property measured based on a prefixed life criterion. The t_F is the time needed to reach this value and is called the lifetime. According to Arrhenius theory, the $K(T)$ in eq. (1) can be expressed as

$$K(T)=Ae^{-E/kT} \tag{2}$$

where E is the activation energy, k is the Boltzmann constant, T is the absolute temperature in Kelvin and A is the proportionality constant. Combining the eqs. (1) and (2) and applying logarithmic functions it becomes

$$\ln t_F = a + b/T \tag{3}$$

where a=ln[$F(P_L)/A$] and b=E/k. A plot of lnt_F *versus* $1/T$ gives a straight line, the intercept of which will give the value of 'a' and the slope will give the value of 'b'.

The main focus of this study is to investigate the effect of thermal ageing on the tensile properties of various flame retardant filled EPDM compounds and apply these effects particularly the variation of elongation at break (EB) to predict the lifetime of the flame retardant filled EPDM compounds.

Experimental

Materials and Preparation of Specimen. EPDM (Nordel 4725, DuPont Dow Elastomers) was used as a rubber matrix. An inorganic FR, Sb_2O_3, was supplied by Sigma Aldrich. Two different organic FRs were selected in this study. They include an aromatic brominated FR; 4,5,6,7-tetrabromo-2-(2-(4,5,6,7-tetrabromo-1,3-dioxoiso-indolin-2-yl)ethyl) isoindoline-1,3-dione

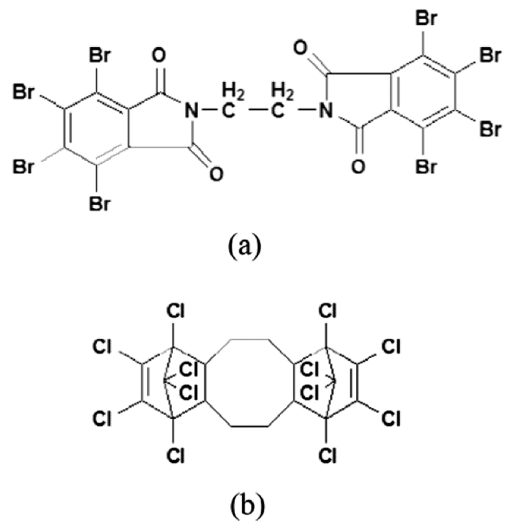

Figure 1. Chemical structure of the halogenated flame retardants (a) Saytex BT-93; (b) Dechlorane plus.

(Saytex BT93), supplied by Albemarle corporation, an aromatic chlorinated FR; 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro1,4,7,10-dimethanodibenzo [a,e] cyclooctene (DelchlornaPlus), supplied by Oxychem. The chemical structures of the FRs are represented in Figure 1. A carbon black (N550, Korea Carbon Black, Korea) was loaded by 50 phr. A conventional sulfur curing system [ZnO: 5 phr, stearic acid: 2 phr, *N*-cyclohexyl-2-benzothiazole sulfonamide (CZ): 1 phr, and sulfur: 1.5 phr] was used. The remaining ingredients for rubber compounds were selected as the typical grade in the rubber industry. The compound composition and designation of major variation components is summarized in Table 1. The compounding procedure is as follows: initially, EPDM was mixed in a Banbury mixer at 140 ℃ for 0.5 min with a rotor speed of 60 rpm using a fill factor of 75%. The various additives including FRs, reinforcing fillers, and processing oils were then added into the rubber and mixed for another 6 min. The curing agents (accelerated sulfur cure system) were added in a two roll-mill (Farrel 8422) at a rotation speed of 15.3 rpm at around 90 ℃ for 10 min. After 24 h, optimum crosslink condition was analyzed by a rheometer (ODR, Alpha Technologies). The optimum conditions were used to vulcanize the prepared samples by a hot-press machine (Caver WMV50H) at pressure of 25 kPa and 170 ℃ temperature.

Characterization. Convection Oven Aging: Various rubber samples of dumbbell-shaped specimens were thermally aged in a convection oven (J-300M, Jisico, Korea) in air at 120, 135, and 150, and 165 ℃ for 1, 50, 100, 300, 500, 700, and 1000 h, respectively.

Tensile Properties and Hardness Measurements: Tensile properties (tensile modulus, tensile strength and elongation at break) of the specimens before and after ageing were measured using a universal testing machine (UTM) (LRX Plus, LLOYD Instrument, USA) at a constant crosshead speed of 500 mm/min as per the ASTM D 412 specifications. The tests were performed at room temperature. Four specimens were tested for each compound to get a reliable result and the results were averaged. Cured samples with a diameter of 30 mm and a thickness of 6 mm were also prepared and measured the indentation hardness (shore A) before and after the thermal ageing.

Results and Discussion

Effect of Thermal Aging on the Tensile Properties and Hardness. Tensile properties of the compounds were evaluated from their respective stress-strain curves to know the effects of thermal ageing on the elastomeric properties at different temperatures over various spans of ageing time. Figure 2 shows the stress-strain behaviour of a representative flame retardant-filled EPDM compound, EP-Sb-Br as a function of ageing time and temperature. For the sake of clarity, the stress-strain behaviour of other compounds has been omitted from Figure 2. It can be seen from the figure that the tensile elon-

Table 1. Major Composition Variables in Compound Recipe Investigated

Ingredient (phr)	Sample designation*					
	EP	EP-Sb	EP-Br	EP-Sb-Br	EP-Cl	EP-Sb-Cl
EPDM	100	100	100	100	100	100
Sb_2O_3		10		10		10
Saytex BT93			50	50		
Dechlorna Plus					50	50

*Sb_2O_3 = Sb, Saytex BT93 = Br, Dechlorna Plus = Cl.

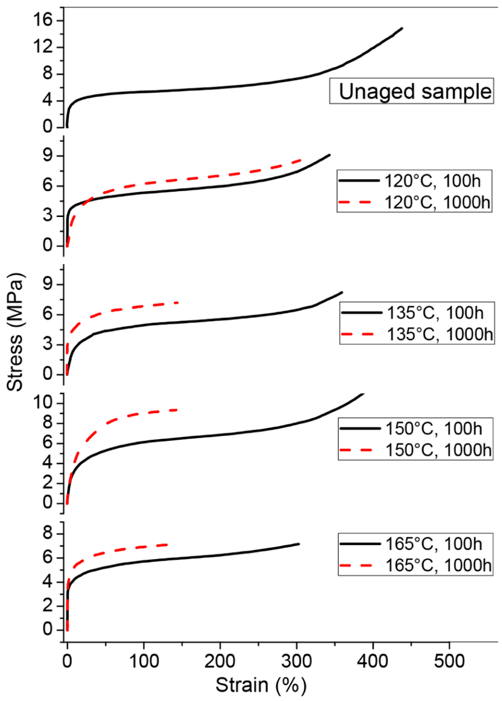

Figure 2. Stress-strain behavior of the compound EP-Sb-Br as a function of ageing time and temperature.

gation is gradually reduced by increasing the thermal ageing time and temperature. The tensile properties such as tensile strength (TS), elongation at break (EB), 100% modulus (M100) and shore-A hardness of all flame retardant-filled EPDM compounds before and after ageing over a range of temperature as a function of ageing time are displayed in Figure 3(a)-(d). To avoid confusion, the property changes of a representative compound EP-Sb-Br measured over a range of temperatures 120, 135, 150 and 165 ℃ is shown in every figure. For all other compounds, the property changes measured only at 150 ℃ is shown to understand the trend. The tensile properties after ageing are represented as a percentage change using the equation:

$$\Delta p = (p/p_0)\times 100 \tag{4}$$

where p_0 is the value of the property before ageing, p is the value of a property after ageing and Δp represents the percentage change in the property. From Figures 3 (a)-(d) it can be seen that the TS and EB of all the compounds decrease with increasing the ageing time and temperature. While the hardness and moduli (M100) were increased. In all our compounds,

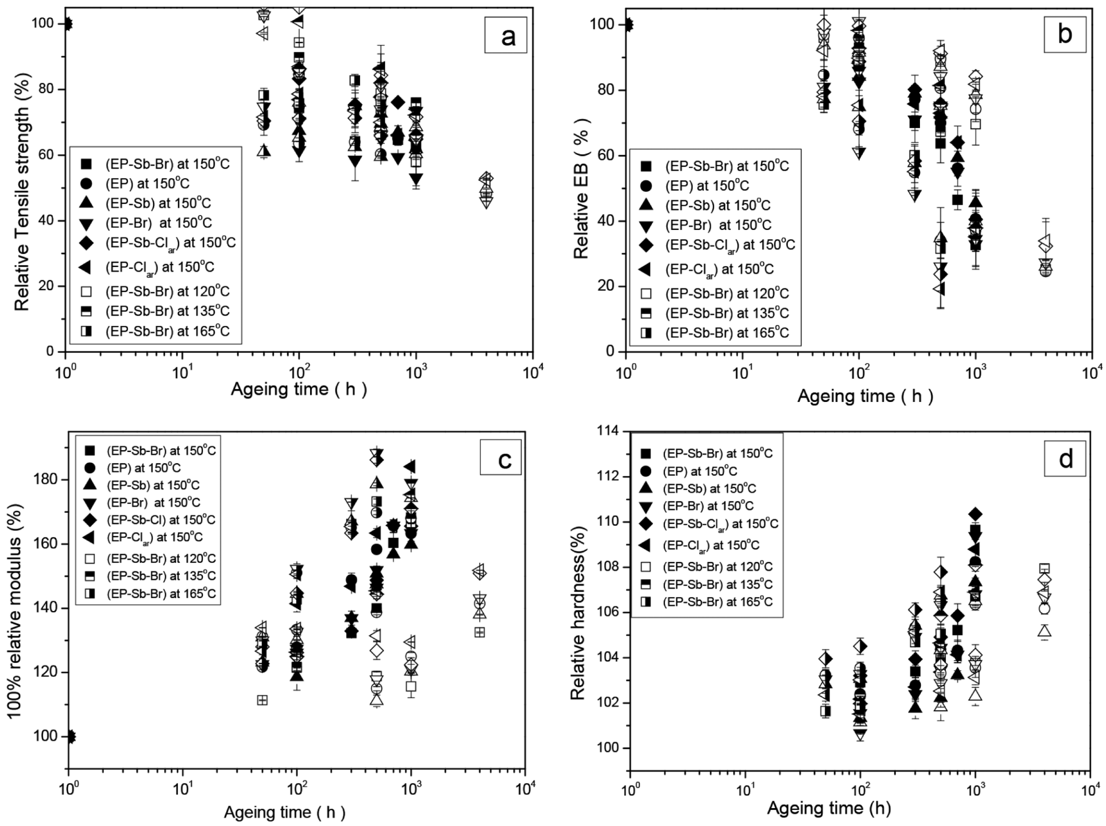

Figure 3. Tensile properties of the compound EP-Sb-Br as a function of ageing time and temperature. (a) tensile strength; (b) elongation at break; (c) 100% modulus; (d) hardness.

we used a conventional sulphur cure system. It has been reported that the conventional sulphur cure system generally crosslink the rubber chains with a higher level of polysulfidic structures with best mechanical properties.[19] It is well known that the polysulfidic crosslinks are less stable (but more flexible) and will break and rearrange to disulfidic to monosulfidic crosslinks upon thermal ageing. The disulfidic or mono sulfidic crosslinks reduce the chain mobility and flexibility.[20] Hence, the lowering of TS and EB observed in our system can be attributed to the restricted movement of the EPDM rubber chains due to the establishment of disulfidic or monosulfidic crosslinks due to thermal ageing. On the other hand, thermal ageing stiffens the EPDM compounds presumably due to the increased crosslink density of the compounds owing to the generation of more monosulfidic crosslinks during prolonged thermal ageing. This may be one of the reasons for the increased modulus and hardness of these EPDM compounds.

Lifetime Prediction Based on the Relative Change in Elongation at Break. The lifetime of all the flame retardant-filled EPDM compounds has been evaluated using the eq. (3). For that, first we experimentally predicted the lifetime of all the FR-filled EPDM compounds by thermal ageing over a range of temperatures 120, 135, 150 and 165 ºC by assuming a 50% relative change in tensile elongation at break as the lifetime criterion or the failure criterion. The lifetime of the compounds thus obtained is plotted against the thermal ageing temperature to get the constants '*a*' and '*b*' for the eq. (3). Figure 4 shows a representative Arrhenius plot of logarithmic lifetime *versus* ageing temperature of the compound EP-Sb-Br. A linear regression analysis was employed to determine the Y-intercept, *a* and the slope, *b*. Likewise, the values of *a* and *b* for all other compounds has been determined and is displayed in Table 2.

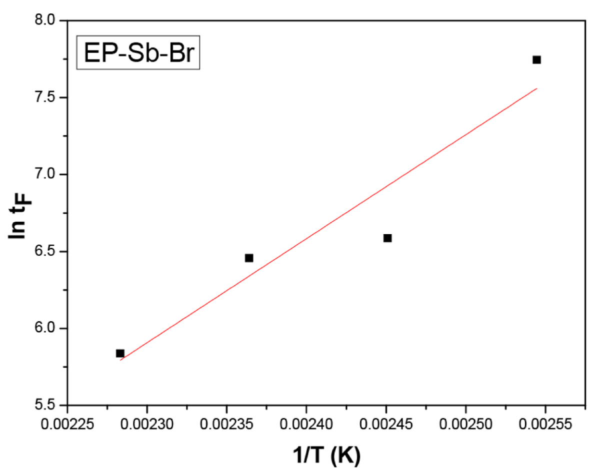

Figure 4. Arrhenius plot of lifetime *vs.* ageing temperature of the compound EP-Sb-Br.

Using these values the lifetime of all the flame retardant-filled EPDM compounds have been extrapolated from room temperature (25 ºC) to 100 ºC to know how many years the material can sustain at a particular temperature. The values thus obtained are shown in Figure 5. From the figure, it can be seen that the predicted lifetime of the FR-filled EPDM compounds follows the order EP @ EP-Sb > EP-Cl > EP-Sb-Cl > EP-Br > EP-Sb-Br. This means that the service life of the EPDM compounds getting reduced in the presence of halogen containing flame retardants. It has been reported that the halogenated flame retardants particularly the brominated compounds are thermally labile and can react with the polymer matrix at elevated temperature in the presence of oxygen.[21-23] As a result, the mechanical integrity of the compound may get

Table 2. Kinetic Parameters Obtained from the Arrhenius Plot of Lifetime against Ageing Temperature by Considering 50% Reduction in EB

Compound	Temp. (ºC)	t_F (h)	Constants of equation $\ln t_F = a+b/T$	
			a	b
EP	165	328	-10.8	7295
	150	774		
	135	963		
	120	2535		
EP-Sb-Br	165	343	-9.6	6757
	150	636		
	135	724		
	120	2309		
EP-Sb	165	398	-10.5	7202
	150	777		
	135	950		
	120	2983		
EP-Br	165	327	-10.0	6918
	150	692		
	135	787		
	120	2323		
EP-Sb-Cl	165	366	-10.2	7067
	150	753		
	135	926		
	120	2643		
EP-Cl	165	335	-10.7	7237
	150	727		
	135	824		
	120	2608		

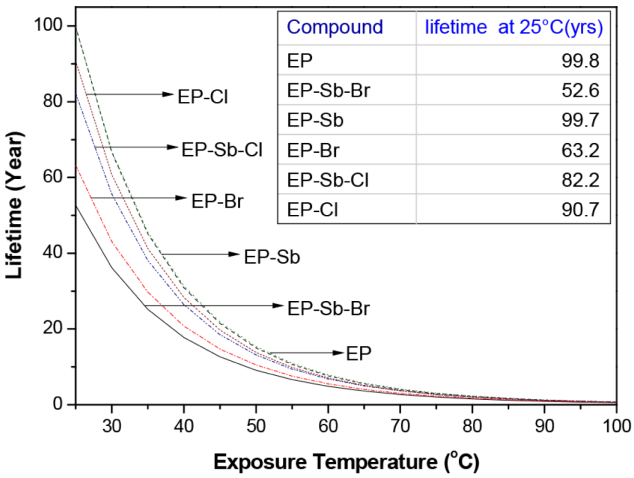

Figure 5. Predicted lifetime of the various flame retardant EPDM compounds at different exposure temperatures.

affected which naturally reduce the lifetime as observed in this study. However, the flame retardant Sb_2O_3 is thermally stable and chemically inactive with the polymer matrix in the absence of halogen containing compounds even at elevated temperature. This may be the reason why Sb_2O_3 alone-filled EPDM compounds show the same lifetime of the base EPDM compound. It is worth mentioning here that, the halogen containing FRs will adversely affect the polymer matrix only at elevated temperature under long exposure time. Hence, the actual lifetime of all these flame retardant-filled EPDM compounds are expected to show more or less similar at the normal service condition.

Conclusions

The effect of thermal ageing and lifetime assessment of various flame retardant-filled EPDM compounds were studied and reported in this paper. The percentage variation of tensile elongation at break of the compounds upon thermal ageing was chosen as a key property parameter to evaluate the lifetime. From the lifetime analysis of the various EPDM compounds it was found that the bare EPDM compound (EP) and its Sb_2O_3 filled one (EP-Sb) showed the maximum lifetime (almost 100 years) at ambient conditions. However, the lifetimes were reduced to 63 years (EP-Br) and 90 years (EP-Cl) when we used brominated and chlorinated materials, respectively, as the flame retardants to the EPDM compound. The predicted lifetimes were found to be reduced again to 53 years and 82 years when we tried a synergistic combination of SB_2O_3 with the brominated (EP-Sb-Br), or chlorinated (EP-Sb-Cl) flame-retardants, respectively.

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