Effects of Sodium Bicarbonate Content and Vulcanization Method on Properties of NBR/PVC Thermal Insulator Foam

P. Suriyachai, N. Thavarungkul and P. Sae-oui

Abstract—In this research sodium bicarbonate (NaHCO₃) was introduced to generate carbon dioxide gas (CO₂) to the existing nitrogen gas (N₂) of elastomeric foam, to lower thermal conductivity (K). Various loadings of NaHCO₃ (0 to 60 phr) were added into the azodicarbonamide (AZC)-containing compound and its properties were then determined. Two vulcanization methods, i.e., hot air and infrared (IR), were employed and compared in this study. Results revealed that compound viscosity tended to increase slightly with increasing NaHCO₃ content but cure time was delayed. The effect of NaHCO₃ content on thermal conductivity depended on the vulcanization method. For hot air method, the thermal conductivity was insignificantly changed with increasing NaHCO₃ up to 40 phr whereas it tended to decrease gradually for IR method. At higher NaHCO₃ content (60 phr), unexpected increase of thermal conductivity was observed. The water absorption was also determined and foam structures were then used to explain the results.

Keywords—sodium bicarbonate; thermal conductivity; hot air method; infrared method

I. INTRODUCTION

ENERGY consumption has recently gained much attention due to rapidly increasing population and changing in life style towards more comfortable lives. Limitation of energy sources causes energy saving become a priority [1]. In big buildings, thermal insulator is normally employed in the heating, ventilation, air-conditioning and refrigerator (HVAC&R) systems. To save more energy, either increasing insulator thickness or using thermal insulators with lower thermal conductivity is recommended [2]. The former, however, is not practically useful because of the higher cost in both the insulator itself as well as the installation. The development of low thermal conductivity insulator is therefore of great interest. Generally, most commercial nitrile rubber (NBR)/poly (vinyl chloride) (PVC) elastomeric thermal insulators possess approximately 95% of gas volume with the thermal conductivity in the range of 0.038-0.040 W/mK at

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mean temperature of 40 °C. In most cases, AZC is used as a blowing agent and thus the decomposed gas embedded in the insulator is mainly N2 gas. As it is widely known that CO2 gas (K=0.014 W/mK) has lower thermal conductivity than N₂ gas (K=0.024 W/mK) [3], many research works used NaHCO₃ as a CO2 generator to develop new materials having low thermal conductivity [4] and improved the foam properties [5]-[8]. It is therefore the aim of this study to lower thermal conductivity of NBR/PVC foam by partially replacing some N2 in the foam with CO2. Moreover, Exxon Chemical International reported that the extrudate profile cured by IR preheating followed by Ultra High Frequency (UHF) possessed smoother surface compared to that cured solely by UHF [9]. Larger cell size is also obtained by IR preheating. As it is widely known that cell size is one of the main factors governing the thermal conductivity of the insulator foam, it is interesting to extend the scope of this study to compare the foam properties obtained from different heating methods. In this work, the effects of NaHCO3 content and vulcanization method on properties, particularly the thermal conductivity, of the foam produced from azodicarbonamide-containing compound were investigated and reported.

II. EXPERIMENTAL

A. Sample Preparation

The compounding formulation used in this study is presented in Table I. All mixing ingredients were used as received. Initially, polymers and other ingredients (except curatives and blowing agents) were mixed in an internal mixer. The dump temperature was about 170°C. After mixing, the compounds were sheeted on a two-roll mill and left at room temperature for 24 hours prior to mixing with the curatives and blowing agents in the second mixing stage. After curing test, the compounds were then extruded into a sheet form using a single screw extruder and finally vulcanized employing either hot air oven or IR methods. For hot air vulcanization, the extrudates were preheated at 136 °C for 12 minutes and then fully vulcanized at 158°C for 12 minutes to form sponge. For IR vulcanization, the compounds were heated, at 158°C for 12 minutes. The quartz infrared was used as an energy source.

TABLE I COMPOUNDING FORMULATION

Ingredient	Supplier	Loading (phr)
Acrylonitrile	Zeon Corporation Co.,	70
Butadiene Rubber	Ltd.	70
Poly (Vinyl Chloride)	TPC Paste Resin	30
Carbon Black (N330)	Thai Tokai Carbon	30
	Product	
Dioctyl Phthalate	Srithepthai	40
Zinc Oxide	Thai-Lysaght Company	5
Stearic acid	Thanachem (Bangkok)	3
Kaolin	Hoffmann Mineral	40
Chlorinated Paraffin	Ineos Asiatic Chemical	12
Talc	Luzenac America INC.	79
Azodicarbonamide	Sopo USA Ltd.	50
Urea	Phonex International	1.5
Sulphur	Rhein Chemie Co., Ltd.	1
Accelerators e.g	Rhein Chemie Co., Ltd.	4
thiuram, mercapto		
Sodium Bicarbonate	Tamaco	Varied
		(0-60)

B. Characterization and Testing

Mooney viscosity of the compound was determined at 135°C using Monsanto Mooney Viscometer (MV2000) according to ISO 289. Cure characteristic at 160°C was measured by EK-2000P rotorless rheometer in accordance with ISO 6502. Decomposition temperatures of the blowing agents when embedded in the compound were studied using Thermogravimetric Analyzer (Mettler Toledo TGA/SDTA 851). The samples were heated from 30 °C to 220 °C with a scanning rate of 3 °C/min under nitrogen atmosphere of 20 psi. Determination of thermal conductivity of the foam was carried out using the Guarded Hot Plate apparatus in accordance with ISO 8302. Porosity was determined by measuring densities of solid and expanded foam and calculated by using (1).

Porosity =
$$1 - (\rho_{foam} / \rho_{solid})$$
 (1)

Where ρ_{solid} is the density of unexpanded compound and ρ_{foam} is the density of expanded foam. Water absorption was measured according to ASTM D1056. Cell structure was studied using Digital BlueTM QX5TM Computer Microscope.

III. RESULTS AND DISCUSSIONS

A. Effects of NaHCO₃ content on Mooney viscosity and cure characteristics

The effect of NaHCO₃ content on Mooney viscosity (ML1+2 @ 135°C), scorch time and cure time is summarized in Table II. Mooney viscosity tended to increase slightly with increasing NaHCO₃ content. This is simply due to the hydrodynamic effect. It is widely known that NaHCO₃ is a

rigid solid and thus it can not deform under external stress. When added into rubber, the proportion of deformable rubber is reduced leading to an increase of compound viscosity. However, the increasing rate of compound viscosity with increasing NaHCO₃ content was very low. This is attributed to large particle size of NaHCO₃. As NaHCO₃ is basic in nature, it should theoretically give enhanced cure rate and thus give shorter cure time for most rubber compounds. The results however revealed that cure time was delayed in the presence of NaHCO₃. Such delay is thought to arise from deactivation of zinc complex by the presence of NaHCO₃.

TABLE II
EFFECT OF NaHCO₃ CONTENT ON THE MOONEY VISCOSITY AND
CURE CHARACTERISTICS OF NBR/PVC BLENDS

Properties	NaHCO ₃ content (phr)			
	0	20	40	60
Mooney Viscosity, (MU)	24.9	26.2	26.2	29.4
Cure Characteristics @ 160 °C				
- Scorch time (min) - Cure time (min)	0.49 1.12	1.11 2.34	1.05 5.44	1.39 4.47

B. Effect of NaHCO₃ content on thermal conductivity

Fig. 1 shows the effect of NaHCO₃ content on thermal conductivity of elastomeric foams achieved from different vulcanization methods. For hot air vulcanization, the addition of NaHCO₃ up to 40 phr had no significant effect on the thermal conductivity of the foam. Further increase of NaHCO₃ content resulted in unexpected increase of thermal conductivity. It is the fact that, at high temperature, NaHCO₃ could release CO2 gas as shown in TGA thermograms (Fig.2) which should give the foam with lower thermal conductivity. In addition, the micrographs shown in Fig. 3 elucidated that the presence of NaHCO3 gave rise to smaller cell size. Theoretically, the existence of CO₂ in the foam structure and the improved cell size should reduce the thermal conductivity. However, the thermal conductivity measured in this study is not significantly changed with increasing NaHCO3 content up to 40 phr. This might be attributed to the counterbalance effect of sodium chloride (NaCl) which is one of the products from the reaction between NaHCO3 and hydrogen chloride (HCl) released from thermal degradation of either PVC or chlorinated paraffin as shown in (2) and (3).

$$NaHCO_3 + HCI \longrightarrow NaCl + H_2CO_3 \qquad (2)$$

$$H_2CO_3 \longrightarrow H_2O + CO_2 (g) \qquad (3)$$

It is widely known that NaCl possesses very high thermal conductivity (K= 6.5 W/mK at mean temperature 16 °C) [10] and thus its presence could result in increased thermal conductivity of the foam. The higher the NaHCO₃ content, the greater the amount of NaCl. To confirm the existence of NaCl, the foam was cut into small pieces and put into boiling water

for 30 minutes. The solution was separated from the samples by filtration and then analyzed by using Ion Chromatography technique. The results are given in Table III. As can be seen, the amount of chloride ion as NaCl increased continuously with increasing NaHCO3 content. At very high NaHCO3 content, even though NaHCO3 resulted in smaller cell size, porosity was obviously decreased when NaHCO3 content was increased from 40 to 60 phr as represented in the Fig. 4. The results implied that dense foam structure was obtained when 60 phr of NaHCO₃ was added into the compound. The effects of dense structure and the high NaCl content were more pronounced than the effect of increased CO2 gas in the foam leading to an obvious increase of thermal conductivity. For IR vulcanization, thermal conductivity tended to decrease gradually with increasing NaHCO3 content until it reached a minimum at 40 phr and then increased thereafter. Since it is accepted that radiation heat transfer is more effective than convection heat transfer [11], IR system therefore gives better heat transfer efficiency than hot air system. Better cure-blow relationship is expected in IR system and thus more CO₂ gas is trapped in the foam leading to larger cell size as depicted in Fig. 5. In this heating system, the effect of CO₂ gas was more pronounced than that of NaCl. Thermal conductivity of the foam therefore decreased slightly with increasing NaHCO₃ content up to 40 phr. Similar to the results in hot air system, at high NaHCO3 content, the thermal conductivity tended to increase. The same explanation is applied.

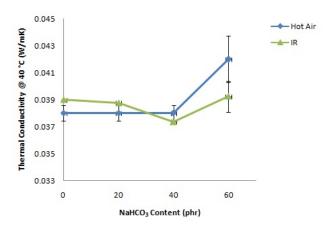


Fig. 1 Effect of NaHCO₃ on thermal conductivity of elastomeric foams achieved from different vulcanization methods.

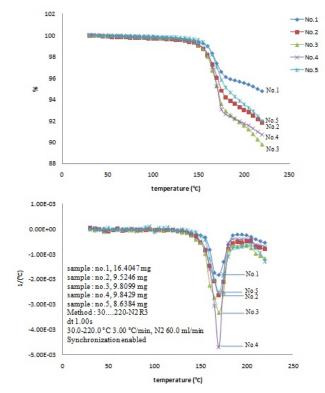


Fig. 2 TGA thermogram of various NBR/PVC compounds (no.1 is NaHCO₃-containing compound, no.2 is AZC and NaHCO₃ 20 phr-containing compound, no.3 is AZC and NaHCO₃ 40 phr-containing compound, no.4 is AZC and NaHCO₃ 60 phr-containing compound and no.5 is AZC-containing compound)

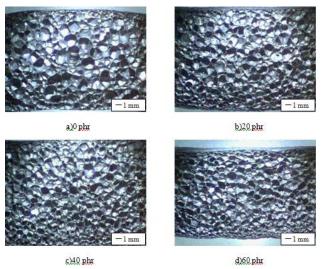


Fig. 3 Cell structure of hot air cured elastomeric foam having different NaHCO₃ loadings (x10)

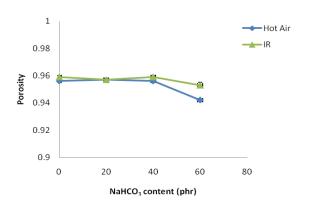


Fig. 4 Effect of NaHCO₃ content on porosity of elastomeric foam

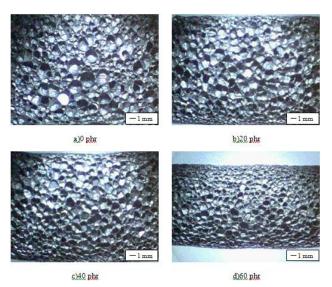


Fig. 5 Cell structure of IR cured elastomeric foam having different $NaHCO_3$ loadings (x10)

TABLE III THE AMOUNT OF NaCl IN RELATION TO NaHCO $_3$ CONTENT

Amount	NaHCO ₃ Content (phr)			
	0	20	40	60
Cl as NaCl (mg/L)	≤1	17	36	37

C. Effects of NaHCO₃ content on water absorption

Since water absorption is one of the main properties of the closed cell foam, determination of water absorption level with increasing NaHCO₃ content is therefore of great interest. Fig. 6 illustrates the relationship between water absorption and NaHCO₃ content. In both vulcanization systems, water absorption increased slightly with increasing NaHCO₃ content until it reaches a maximum at 40 phr and then decreased afterwards. As can be seen in Fig. 3 and 5, increasing NaHCO₃ content from 0-40 phr leads to the reduction of cell size.

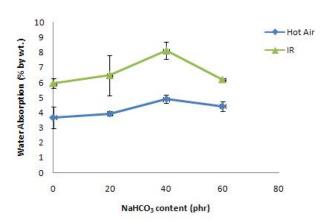


Fig. 6 Effect of NaHCO₃ content on water absorption of elastomeric foam

Without significant change of porosity, the reduced cell size brought about the increase of surface area for water absorption. As a consequence, water absorption was initially increased with increasing NaHCO₃ content up to 40 phr. However, at 60 phr of NaHCO₃, the dense structure due to low porosity caused the reduction of water absorption. At any dosage of NaHCO₃, water absorption of the foam obtained from IR system was greater than that obtained from hot air system. This is simply due to the higher porosity.

IV. CONCLUSIONS

The addition of NaHCO₃ into AZC-containing compound caused increases of both Mooney viscosity and cure time. The relationship between thermal conductivity and NaHCO₃ content was dependent on the vulcanization method, i.e., thermal conductivity was unchanged with increasing NaHCO₃ up to 40 phr for hot air vulcanization whereas it tended to decrease gradually for IR vulcanization. However, at higher loading of NaHCO₃ (60 phr), thermal conductivity of the foam was sharply increased, regardless of the vulcanization method, due to the presence of NaCl and dense foam structure. Water absorption of the foam obtained from both vulcanization systems tended to increase slightly with increasing NaHCO₃ content up to 40 phr. At higher loading of NaHCO₃, water absorption was decreased due to the dense foam structure.

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