CHAPTER 8

Thermal Conductivity Of Carbon black Filled Ethylene-Octene Copolymer And It’s Microcellular Foams
Chapter 8: Thermal Conductivity of Carbon Black Filled Ethylene-Octene Copolymer and it’s Microcellular Foams

8.1 Introduction

Cellular materials are widely used as thermal insulator in residential, commercial, and industrial application at low-ambient temperature range due to its superior thermal insulation property. Thermal conductivity is one of the most important functional parameters in the applications and use of cellular polymers. The polymer foams are used as excellent thermal insulator due to their cellular structure which reduces the material cost and thermal conductivity of the material [311]. The heat transfer through carbon black filled solid and porous polymer composites have been investigated by several researchers. It has been reported that the thermal stability of the rubber composites improves by loading of carbon black as filler in rubber [113]. The transverse and axial thermal conductivity of a carbon black composite has already been studied [112]. The thermal conductivity of PDMS-CB composite has been studied and reported that thermal decomposition of the PDMS composite is retarded due to the presence of carbon black filler [312]. Benli et al. [114] reported that the incorporation of carbon black as filler affected the thermal conductivity of polyurethane elastomer. Also the thermal conductivity of cellular elastomer is affected significantly when reinforced by carbon black. It is reported that a closed cell rigid polymer foam containing at least about 2 % by weight of carbon black as filler, which reduces the aged k-factor of the foam to below the aged k-factor of the corresponding unfilled foam [205]. Also 2 wt % carbon black filled polyisocyanate and an isocyanate compound has aged k-factor less than that of unfilled foam [206]. Various theoretical models have been employed for prediction of thermal conductivity of foamed materials [313-315]. It is reported that the thermal conductivity of unfilled and aluminium silicate, CaCO₃ and silicate filled closed cell microcellular ethylene octene copolymer foam reduces as the volume fraction of the solid reduces [209]. This chapter deals with the thermal conductivity of carbon black filled closed cell microcellular ethylene octene copolymer with reference to filler as well as blowing agent concentration. The thermal conductivity of the microcellular foams have been predicted and evaluated by different theoretical models.
8.2 Results and Discussion

8.2.1 Thermal conductivity of EOC/CB vulcanizates and their microcellular foams as a function of carbon black and blowing agent concentration

The cellular polymers can be considered to be a two-phase mixture of gas and solid polymer in which the gas is dispersed in a continuous matrix, either in discrete bubbles or in interconnected cavities. Figure 8.1 depicts the thermal conductivity of the unfilled and carbon black filled microcellular ethylene octene copolymer vulcanizates with variation of carbon black and blowing agent loading. It is observed that the thermal conductivity increases with increase in carbon black loading in case of solid vulcanizates. This trend of variation in thermal conductivity is also reported in other studies [316, 317]. However, increase in blowing agent loading leads to reduction in thermal conductivity. This reduction is due to the effect of the gas inside the cells and is usual for cellular materials.

![Figure 8.1](image-url)  
*Figure 8.1* Variation of thermal conductivity of microcellular ethylene octene copolymer vulcanizates as a function of carbon black and blowing agent loading at 30°C.
It is interesting to note that at a given load of blowing agent thermal conductivity decreases with increase in carbon black loading. This is due to the nucleation effect of CB, i.e., with increase in CB loading the cell density increases and thus the volume of air in the samples increase which reduces the thermal conductivity.

Figure 8.2 shows variation of relative thermal conductivity with relative foam densities. It is observed that relative thermal conductivity decreases with relative foam density. With increase in relative density (ratio of foam density $\rho_f$ of the vulcanizate to the density of the solid material $\rho_r$), the cell wall becomes thicker, leading to increase in relative thermal conductivity (thermal conductivity of the foam divided by conductivity of the solid) which is attributed to reduced thermal radiation or increased thermal absorption. For example the relative thermal conductivity decreases from 1 to 0.51 W m$^{-1}$ K$^{-1}$ with decrease in relative density of 20 phr carbon black filled microcellular vulcanizates from 1 to 0.23.
Figure 8.3 Variation of thermal conductivity with average cell sizes of unfilled and carbon black filled microcellular vulcanizates at 30°C.

Figure 8.3 shows variation of thermal conductivity with average cell size of unfilled as well as carbon black filled microcellular vulcanizates. It is observed that in unfilled vulcanizates thermal conductivity decreases with decrease in cell sizes however a clear trend of variation in thermal conductivity with average cell sizes is not observed in case of CB filled microcellular vulcanizates.

8.2.2 Thermal conductivity of EOC/CB vulcanizates and their microcellular foams as a function of temperature

Figure 8.4 depict the thermal conductivity of unfilled ethylene octene copolymer vulcanizates. It is observed that in case of unfilled vulcanizates a decreasing trend of thermal conductivity is observed with increase in temperature studied. This decreasing trend with rise in temperature has also been observed in case of silica/carbon black filled microcellular EPDM rubber [318]. The reduction in the thermal conductivity of the unfilled systems can be explained based on free volume theory. Increase in temperature enhances the free volume theory. The increased free volume decreases the inter-chain coupling which results in the
increase in the resistance to energy transfer between the molecules [319]. As a consequence the thermal conductivity is reduced with rise in temperature.

![Graph showing thermal conductivity vs. temperature](image)

**Figure 8.4** Thermal conductivity of unfilled solid and foamed ethylene octene copolymers at different temperatures.

Figure 8.5 and 8.6 show the thermal conductivity of 20 and 40 phr carbon black filled ethylene octene copolymer vulcanizates. It is observed that thermal conductivity increases marginally with increase in temperature. Though it has been reported in some studies that the thermal conductivity of open cell [320] and closed cell polyolefin foams synthesized by a high pressure gas solution process [321] increases with increase in temperature. This can be explained on the fact that with increase in temperature the molecules of material will absorb this heat energy and thus increase the capacity of oscillation about the equilibrium position, clash the environs of the molecules gain energy particles that make them oscillate with a capacity greater than it was the clash of these molecules in turn with its neighboring other molecules gain energy, and thus we believe that the heat transmitted through the vibration of molecules without moving from the position of equilibrium [322].
CHAPTER 8

THERMAL CONDUCTIVITY OF CARBON BLACK FILLED ETHYLENE-OCTENE COPOLYMER AND IT’S MICROCELLULAR FOAMS

Figure 8.5 Thermal conductivity of 20 phr carbon black filled solid and foamed ethylene octene copolymers at different temperatures.

Figure 8.6 Thermal conductivity of 40 phr carbon black filled solid and foamed ethylene octene copolymers at different temperatures.
8.2.3 Theoretical modeling of thermal conductivity

Heat transfer in cellular materials are based on four mechanisms i) conduction through the gas phase, ii) conduction through the solid phase, iii) gas convection and iv) radiation. The heat convection does not occur when the cell size is smaller than 3mm [204] and heat transport across in the open or closed cell foam is carried by conduction along the polymer matrix, conduction across the gas phase and thermal radiation.

![Graph](image.png)

**Figure 8.7** Variation of thermal conductivity of the unfilled and carbon black filled EOC and their foams with volume fraction of the solids at 30°C.

According to Kenner’s equation, [323] based on the result of Maxwell and proposed for polymer composite consists of discrete particles randomly distributed in a continuous phase is

\[
k_c = k_g \left( \frac{k_s (2V_1 - 1) + 2k_g (1 - V_1)}{k_g (1 - V) + k_s (2 + V_1)} \right) \]

[8.1]

Where \( k_c \) is the conductivity of the composite, \( k_s \) and \( k_g \) are the conductivities of the continuous (solid) and discrete (gas) phase respectively; \( V_1 \) is the volume fraction of the discrete or gas phase; and \((1-V_1)\) is the volume fraction of continuous or solid phase. The volume fraction of the gas phase is calculated from the following expression [323]
\[ V = \frac{\rho_s - \rho_f}{\rho_s - \rho_g} \]  

[8.2]

Where \( \rho_s \) is the density of the solid, \( \rho_f \) is density of the foam and \( \rho_g \) is the density of the gas (air).

Figure 8.7 shows the thermal conductivity values of the unfilled and carbon black filled EOC and their foams as a function of volume fraction of the solids at 30\(^\circ\)C. It is observed that the thermal conductivity decreases with decrease in volume fraction of the solids, which is attributed presence of air bubbles. It can also be observed that the experimental results are greater than the theoretical model. The greater experimental values obtained may be attributed to stretching of polymer matrix during expansion due to which the thermal conductivity increases in the direction of orientation because of the alignment of the polymer molecules [319].

### 8.3 Conclusions

The thermal conductivity of the carbon black reinforced solid and closed cell microcellular ethylene-octene copolymer vulcanizates have been studied as a function of carbon black and blowing agent loading at 30\(^\circ\)C, 40\(^\circ\)C and 50\(^\circ\)C. It has been observed that the thermal conductivity increases with carbon black loading for filled solid vulcanizates due to formation of conductive network. It is also observed that the thermal conductivity decreases with increase in blowing agent i.e., decrease in relative density of the closed cell microcellular vulcanizates at a particular filler loading. The thermal conductivity values of foamed vulcanizates are found to be lower than that of solid vulcanizates. The relative thermal conductivity also reduces with reduction in relative density. A decreasing trend in the thermal conductivity with average cell size is observed in unfilled vulcanizates but a clear trend is not obtained in case of CB filled microcellular vulcanizates. With increase in temperature, the thermal conductivity decreases for unfilled microcellular foams due to the increase in free volume. However, in case of CB filled vulcanizates the thermal conductivity increases marginally with increase in temperature. The results reveal that the thermal conductivity (k) of microcellular ethylene-copolymers does not follow the theoretical model equation. The experimental thermal conductivity values are found to be higher than that of the theoretical values. This can be attributed to the stretching of polymer matrix during expansion.