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# Photo-induced crosslinking of ethylene propylene diene monomer (EPDM) by buckminsterfullerene

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Summary

An EPDM (ethylene-propylene ethylidene norbornene terpolymer) rubber has been dissolved in o-dichlorobenzene with 5 phr of $C_{60}$. A cast film which is kept in the dark remains soluble, while exposure to light results in a crosslinked film.

## Introduction

Previously[1], we reported dissolving EPDM in o-dichlorobenzene (o-DCB) with a small amount of buckminsterfullerene, $C_{60}$. When cast onto a glass slide and the solvent evaporated, an insoluble elastic film formed at room temperature. We now have discovered that the crosslinking occurs only after exposure to light. Indeed, others[2–5] have reported on the photochemistry of $C_{60}$. In reference 1, the exposure to ambient light was inadvertent. In this communication, EPDM/$C_{60}$ films were prepared, given controlled exposure to ultraviolet light, and then characterized for crosslinking.

## Experimental

The EPDM and EPR were obtained from Exxon (Vistalon 2200, 2.3% ENB; Vistalon 606, saturated). The $C_{60}$ was purchased from the Materials and Electrochemical Research Corporation (Tucson, AZ). The ultraviolet light source was 6w at 365 nm.

Preparation: 1.00 g of EPDM was dissolved in 23 ml, of o-dichlorobenzene at 100–120°C under nitrogen for 5 hours to produce a colorless solution, which was allowed to cool to room temperature. Then, 0.05 g of $C_{60}$ was added. Another 2 mL of o-DCB were added to rinse the neck of the mixing flask, which had been wrapped in aluminum foil to prevent exposure to light. Mixing under nitrogen continued for 1 day, before pouring the solution into two petri dishes, which were then placed in a dark vacuum oven to dry at room temperature. Dried film thickness was about 0.1 mm.

Exposure to light took place inside a closed chamber with an ultraviolet light source attached to the ceiling. Using a radiometer, the light intensity at the position of the exposure of the films was about 200–230 $\mu w/cm^2$.

Crosslink density was determined from equilibrium stress-strain measurements using the Mooney-Rivlin method, as described in reference 1. Three specimens were tested for each case.

Results and Discussion

Films were tested for solubility in benzene before exposure to light and after exposure times of 48, 96 or 192 hours. Films which were kept in the dark for one week remained soluble, even if they previously had been heated to 180°C for several hours. However, films which had been exposed to the light became insoluble. Table 1 gives crosslink densities for different exposure times. Figures 1 and 2 show equilibrium stress-strain results plotted in the normal and Mooney-Rivlin fashion, respectively. The upturn in both plots at high extension is indicative of crosslinking.

Although the films have clearly crosslinked after exposure to light, the crosslinking may not be uniform, since intensity will be reduced as the light penetrates the films. Thus, crosslink densities are "effective" averaged values.

Films also were prepared with ethylene-propylene rubber (EPR) which contained 5 phr of $C_{60}$. As expected, these films remained soluble in benzene even after exposure to light, thus confirming that the crosslinking site of the EPDM was the ethylidene norbornene unsaturation.

Table 1. Crosslink densities after various exposure times to ultraviolet light

| Exposure time (hr) | Crosslink density (mol/m$^3$) |
|---|---|
| 48 | 0.363±0.040 |
| 96 | 1.252±0.146 |
| 192 | 3.029±0.210 |

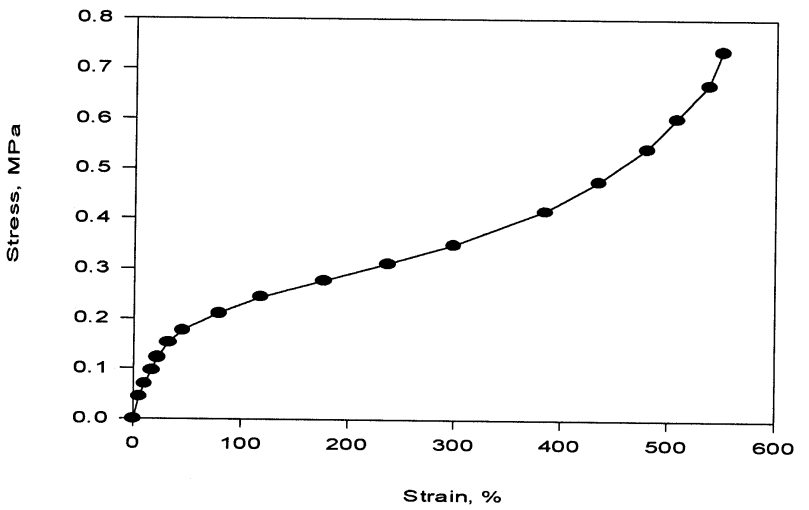



Figure 1. Equilibrium stress-strain curve for EPDM/$C_{60}$ after 192 hours of exposure to ultraviolet light.

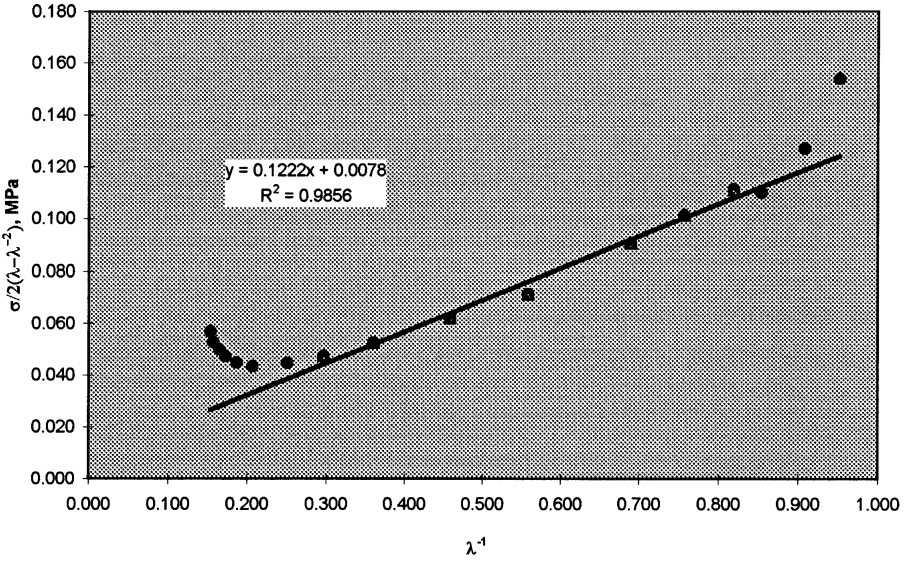
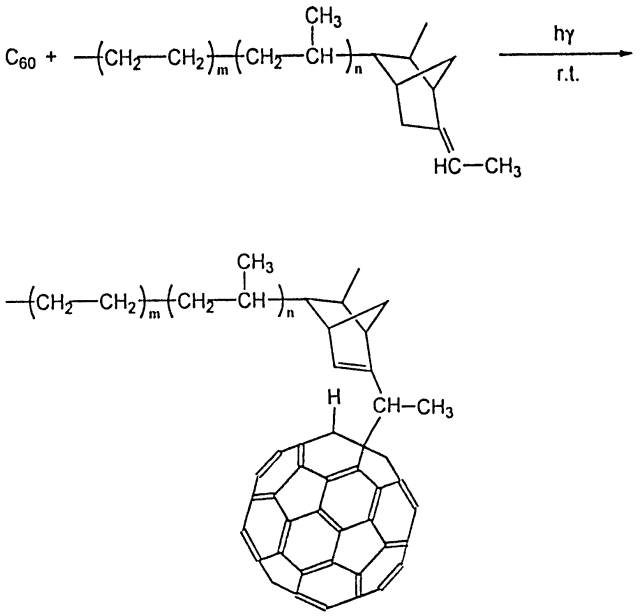



Figure 2. Mooney-Rivlin plot of data in Figure 1.

The mechanism of crosslinking may involve an ene reaction, like that which has been proposed[6] for the reaction between $C_{60}$ and 3-methylene-2,3-dihydrofuran. Scheme 1 is thus proposed.




Scheme 1.

Reaction may be favored by the triplet excited state of buckminsterfullerene, $^3C_{60}$*, which is induced by ultraviolet light[7]. $^3C_{60}$* is a stronger electron acceptor, i.e., more electron deficient, then $C_{60}$.

Reference

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