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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 1 phr of C_{60}. When cast onto a glass slide and dried, an insoluble film exhibiting reversible elasticity forms.

Introduction

The chemical properties of buckminsterfullerene, C_{60}, have been widely studied in recent years (1). C_{60} is attacked by nucleophiles and amines are known to add to fullerene double bonds (2). Furthermore, C_{60} has been shown to react with free radicals (3), and to undergo cycloaddition with dienes (4). Surprisingly, we show here that C_{60} is able to cause crosslinking of ethylene propylene diene monomer (EPDM), where ethylidene norbornene (ENB) is the diene (ter) monomer.

Experimental

The EPDM was obtained from Exxon (Vistalon 2200, 2.3% ENB), while the C_{60} was purchased from the Materials & Electrochemical Research Corporation (Tucson, AZ).

Preparation 1: 0.6034g of EPDM was dissolved in 10 mL of o-dichlorobenzene at 100-110°C for 2-3 hours, resulting in a 4% by weight colorless solution. (o-dichlorobenzene was selected because it is a relatively good solvent for C_{60} (5)). Now, 0.0060 g of C_{60} was added to the solution, which was stirred at 105°C for 4 hours. The transparent, colorless solution became a transparent, magenta colored solution. This color is characteristic of dissolved C_{60} (6). The solution was cast onto a glass slide and dried for 11 hours. Further

solvent removal was carried out in a vacuum oven at 58°C for about 6 hours. Films were stored for four days in a lab drawer before stress-strain and swell testing.

Preparation 2 was made in the same way as Preparation 1, except no C_{60} was added.

Crosslink density, ρ_c, was determined from equilibrium swelling data, employing the Flory-Rehner equation (7):

$$\rho_c = -\frac{1}{2V}\left[\frac{\ln(1-v_r)+v_r+\chi v_r^2}{v_r^{1/3}-\frac{v_r}{2}}\right]$$

where,

V = molar volume of swellant
v_r = volume fraction of rubber in swollen gel
χ = interaction parameter

For EPDM, $\chi = 0.354 + .083\ v_r$ in heptane and $\chi = 0.488 + 0.271\ v_r$ in benzene (8). Swelling time was one day. Swollen films were weighed and then dried for one day at room temperature in a hood. The dried gel was weighed, allowing v_r to be calculated.

Crosslink density also was determined from equilibrium stress-strain measurements. A strip sample with gauge marks was loaded with a small weight, and after 30 minutes, the deformation monitored with a cathetometer. The process was repeated for increasing loads, and stress-strain values determined. A Mooney-Rivlin determination of ρ_c was made by plotting $\sigma/[2(\lambda-\lambda^{-2})]$ versus $1/\lambda$:

$$\rho_c = \frac{C_1}{RT},$$

where C_1 is the intercept of the Mooney-Rivlin plot; R is the gas constant; T is the absolute temperature.

Results and Discussion

Preparation 1 containing 1 phr of C_{60} resulted in a yellow-brown, transparent film which was swollen by, but was insoluble in, benzene and heptane after one day of swelling. When the unswollen

film was held by hand in the stretched state, and then released, the film snapped back to its original dimensions, indicating the formation of a three-dimensional network. Crosslink density, ρ_c, with heptane or benzene as swellants, was 2.7 or 2.5 mole/m^3, respectively.

Stress-strain curves of three samples of Preparation 1 were determined; responses were similar. Figure 1 gives results for one of the samples, while Figure 2 shows the corresponding Mooney-Rivlin plot. Data were fitted with a least-squares straight line and, from the calculated intercept, ρ_c=6.2 ± 0.5 mole/m^3.

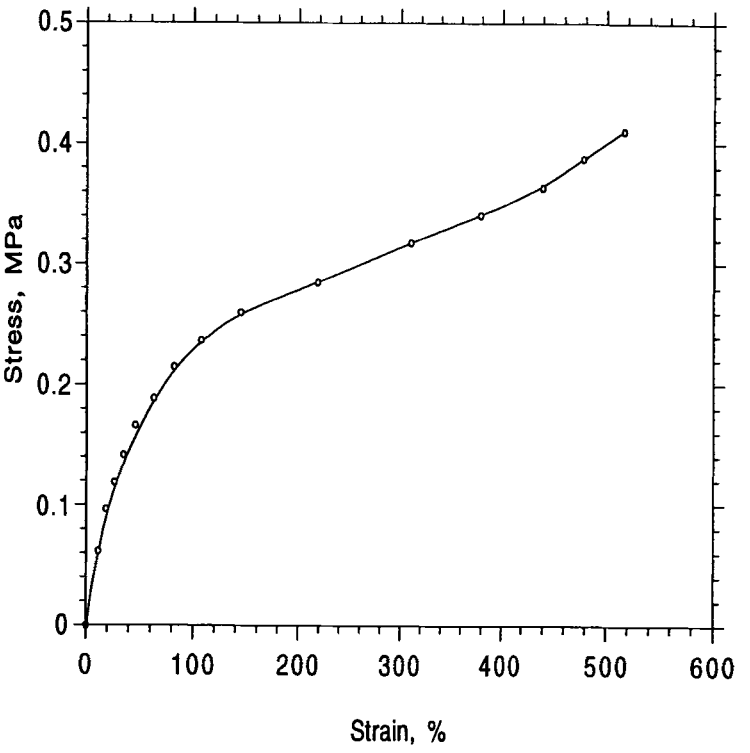


Figure 1. Equilibrium stress-strain curve for Preparaton 1 (EPDM with 1 phr of C_{60}).

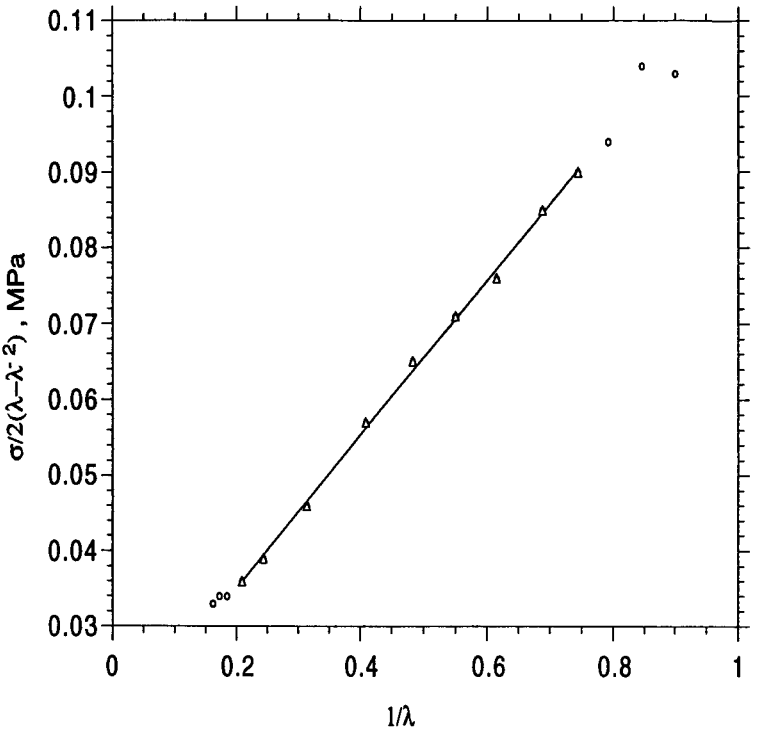
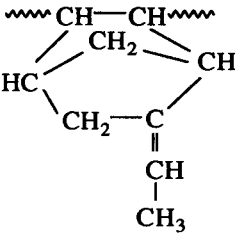


Figure 2. Mooney-Rivlin plot corresponding to Figure 1. o, Δ (all data); Δ (least squares fitted for intercept determination).

Preparation 2, with no added C_{60}, was a soft, colorless film, which "necked down" and deformed irreversibly when stretched. The film readily dissolved after a few minutes in benzene or heptane, just like the "virgin" EPDM.

EPDM is a terpolymer of ethylene, propylene, and ethylidene norbornene (ENB). The structure of the ENB unit in the terpolymer:



Presumably, crosslinking is involved with the pendent unsaturation of the ENB, but the authors are unaware of previous literature demonstrating the reaction of C_{60} with a simple double bond. Further experiments are underway to probe this possibility using model, unsaturated compounds, as well as experiments with EPR (ethylene-propylene rubber with no unsaturation) to test the hypothesized role of the ENB.

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