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Proton spin–spin relaxation and n.m.r. imaging of peroxide/coagent crosslinked *cis*-1,4-polyisoprene

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

Proton T_2 relaxation and n.m.r. imaging experiments were utilized to study the molecular mobility and heterogeneity of *cis*-1,4-polyisoprene crosslinked with dicumyl peroxide in the presence of triallyl cyanurate (TAC) and zinc diacrylate (ZDA) as coagents. It was observed that the long T_2 relaxation times of the rubber protons in peroxide/TAC or peroxide/ZDA crosslinked elastomers decrease with the increase in the crosslink density resulting from the addition of peroxide or coagent. The T_2 relaxation times of protic solvent in swollen rubber are also affected by the physical property changes of the networks induced by peroxide and coagent addition. It was concluded that the solvent T_2 relaxation times depend on solvent-polymer interactions as well as the crosslink density of the networks. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: n.m.r. imaging; Relaxation; Crosslinking

1. Introduction

The use of proton n.m.r. techniques to analyze the motional behavior of elastomeric systems has been widely utilized in recent years. One technique used extensively is spin–spin (T_2) relaxation measurements. T_2 measurements probe the kilohertz motional regime, which is the frequency range of longer range cooperative motions. These motions are highly affected by crosslinking reactions and the dispersion of the network junction points. Applications of T_2 measurements to elastomers have included analysis of dispersion of carbon black in rubber [1,2], real-time measurement of solvent diffusion into elastomers [3], analysis of crosslinked elastomers [4–10], measurement of T_2 behavior as a function of temperature [11], analysis of domain size in blends [12], and spatial analysis of swollen networks [13].

As another tool in structural analysis, proton n.m.r. imaging (NMRI) is useful for two- and three-dimensional analysis. Proton NMRI is used to study the chemical and motional heterogeneity in the crosslinked elastomeric networks. Samples are often swollen in an appropriate solvent [14,15] to enhance greater segmental mobility and extensibility. The main advantage of this technique is its ability to map spatially a wide variety of structures, using both static and dynamic parameters [16]. The spatial mapping and contrast capabilities of NMRI have created natural incentives for exploiting the technique in the field of elastomers [13,17–21] and solid samples [22,23] For the study of the molecular mobility of the polymer chains, the NMRI technique provides a sensitive probe of the nuclear environment [24]. The variety of characteristic motions can be interpreted in terms of relaxation parameters which include spin–lattice relaxation (T_1) and spin–spin relaxation times (T_2). The detection of internal voids, defects, and inhomogeneity constitute important applications for NMRI. This category of morphological investigation typically relies on the n.m.r. signal acquired from a protic solvent imbibed in the sample.

The goal of this study is to evolve a better understanding of structure/property relationships in a peroxide/coagent crosslinked elastomer. Peroxide/coagent curing is desirable in applications where creep resistance at high temperatures is required. An important feature of peroxide/coagent crosslinking is the superior strength of the C–C bond compared to the S–S or C–S bonds in sulfur curing. The stronger bond strengths result in superior heat resistance characteristics compared to sulfur crosslinked systems. The experimental techniques of proton T_2 relaxation and proton n.m.r. imaging

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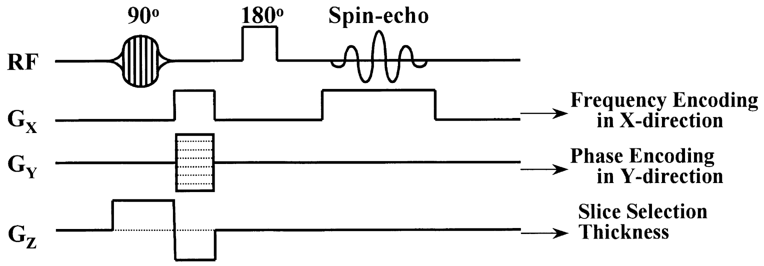

Fig. 1. The block diagram of the Carr–Purcell spin-echo pulse sequence. Slice selection is accomplished with the selective 90°pulse and the G_z gradient, while the G_x gradient is the frequency encoding and read gradient and the G_y is the phase encoding gradient.

were utilized to analyze peroxide/coagent crosslinked elastomeric networks.

2. Experimental

Cis-1,4-polyisoprene (PI, Natsyn 2200) was blended with peroxide and coagent in a Brabender Mixer. Dicumyl peroxide (DCP, Aldrich Chemical Co.) was used as a curing agent and triallyl cyanurate (TAC) and zinc diacrylate (ZDA) (Aldrich Chemical Co.) were used as curing coagents. Peroxide concentrations were varied from 2 to 20 phr at a coagent concentration of 10 phr. Also, coagent concentrations were varied from 0 to 20 phr at a peroxide concentration of 5 phr. The blended samples were crosslinked on a Carver Hot Press for 75 min at 150°C under a pressure of 280 lbs/in^2. After the completion of curing, the samples were quenched in a cold water.

Equilibrium swelling measurements were performed with the solvent cyclohexane. A small piece of the sample was soaked in the solvent in a glass vial with stopper and left in the dark for 24 h. The samples were removed, blotted dry with a paper towel, placed in a clean stoppered vial and weighed. The samples were dried for 24 h in a vacuum oven at 60°C and then reweighed to obtain the weight of the network and the amount of imbibed solvent.

Prior to the imaging experiment the crosslinked samples were swollen with cyclohexane. Swollen rubber samples were cut into 12 mm diameter disks and kept with the solvent in vials. All samples were imaged at ambient temperature on a Bruker MSL 300 spectrometer (proton frequency of 300.13 MHz). The samples were contained in 14.5 mm glass tubes and were positioned vertically in the instrument's microimaging probe which was equipped with a saddle-type radio-frequency coil of 15 mm diameter. The images were obtained by a standard CPMG spin-echo (selective 90°/phase-shifted, non-selective 180°) pulse cycle. Schematic diagrams of the imaging pulse sequence are shown in Fig. 1. The slice thickness was approximately 1 mm and was performed by using a magnetic field gradient in the *z*-direction during the selective 90° pulse. A spectral width of 62 500 Hz was used in the acquisition. Four per phase encoding steps were signal averaged in producing each image, using 90° increment (x, $-y$, $-x$, y) phase cycling. The images contained 256 × 256 pixels with a spatial resolution of 78 μm per pixel. All images were transferred to SGI UNIX station using an Ethernet network. Data processing was performed using Tripos IMAGE software.

Proton T_2 experiments were performed with CP/MAS probe on a Bruker MSL 300 using the Carr–Purcell spin-echo sequence. Eight scans were accumulated for each spin-echo time with a recycle delay of 3 s. The spectral endpoints were set using a previous literature value of 5.1 ppm for the olefinic proton resonance. The FIDs were acquired with the spinning rate of 3.5 kHz for solid samples and with no spinning for solvent-swollen samples.

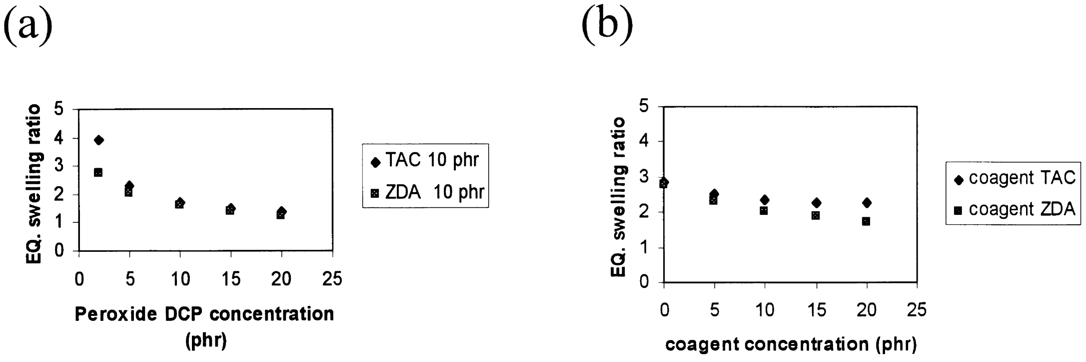

Fig. 2. The equilibrium swelling measurements of peroxide/coagent crosslinked samples (swelling solvent, cyclohexane): (a) peroxide concentration is varied at coagent, 10 phr and (b) coagent concentration is varied at DCP, 5phr.

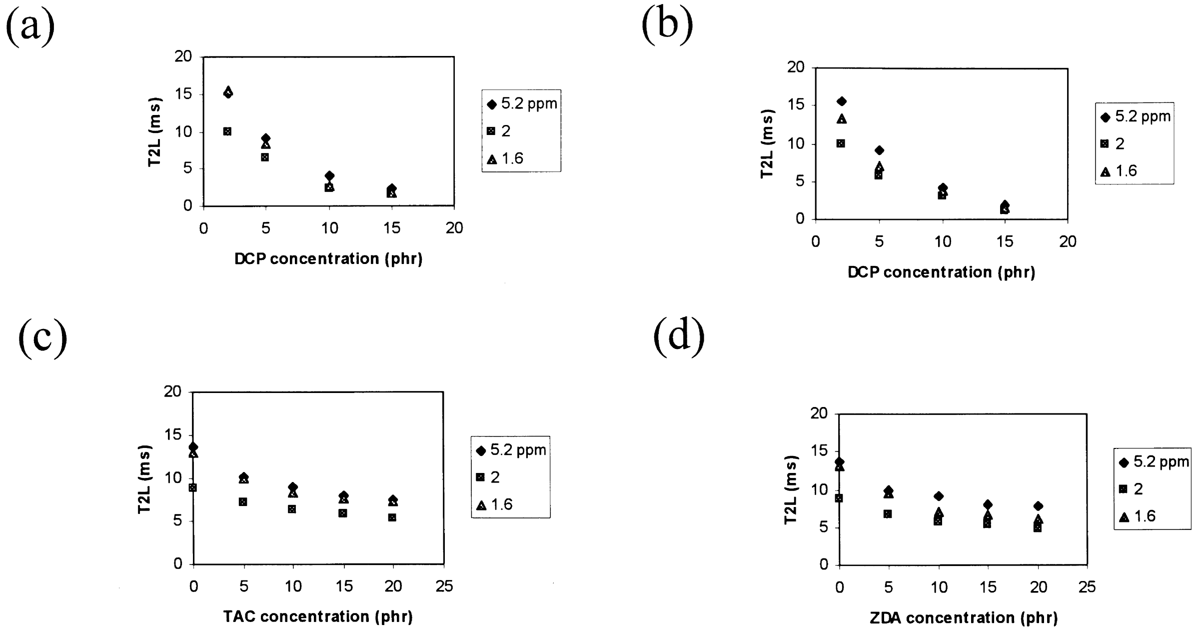

Fig. 3. The proton T_{2L} relaxation times of peroxide/coagent crosslinked *cis*-1,4-polyisoprene: (a) PI/TAC blends and (b) PI/ZDA blends with peroxide variation at coagent, 10 phr; (c) PI/TAC blends and (d) PI/ZDA blends with coagent variation at DCP 5 phr. The T_{2L} relaxation times of one olefinic protons and two aliphatic protons were measured, respectively. The decrease in the relaxation times were observed with the increase in the peroxide or coagent concentration.

3. Results and discussion

Fig. 2 shows the results of the equilibrium swelling measurements with the solvent cyclohexane. A decrease in the equilibrium swelling ratio was observed with an increase in the peroxide concentration. (Fig. 2(a)) The higher crosslink density obtained from higher peroxide concentration results in the lower swelling ratio. Fig. 2(b) shows the decrease in the swelling ratio with the increase in the coagent concentration, suggesting the formation of additional crosslinks in the networks by the addition of coagent. A change in the polymer-solvent interaction parameter due to copolymerization can also contribute to the decrease in the swelling ratio. The ZDA coagent systems show lower swelling ratio values than the TAC coagent systems.

Proton T_2 relaxation measurements were performed with a CP/MAS probe at a spinning rate of 3.5 kHz. (Fig. 3) With magic angle spinning, each molecule experiences a continuous series of orientations with respect to the external

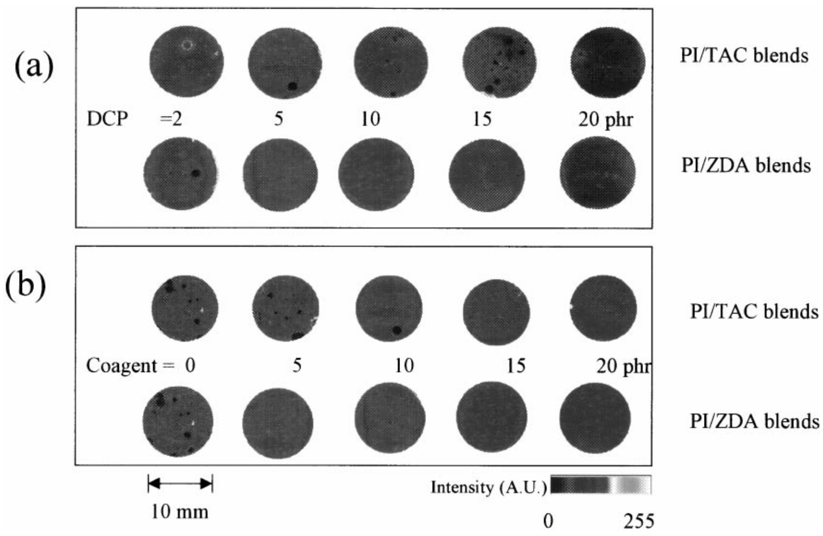

Fig. 4. The solvent spin-echo images of the crosslinked networks swollen in cyclohexane: (a) peroxide (DCP) concentrations were varied as indicated while the coagent concentration was held constant at 10 phr and (b) coagent (TAC or ZDA) concentrations were varied as indicated while the peroxide (DCP) concentration was held constant at 5 phr. The images were acquired using a spin-echo time of 7 ms and a repetition time of 3 s.

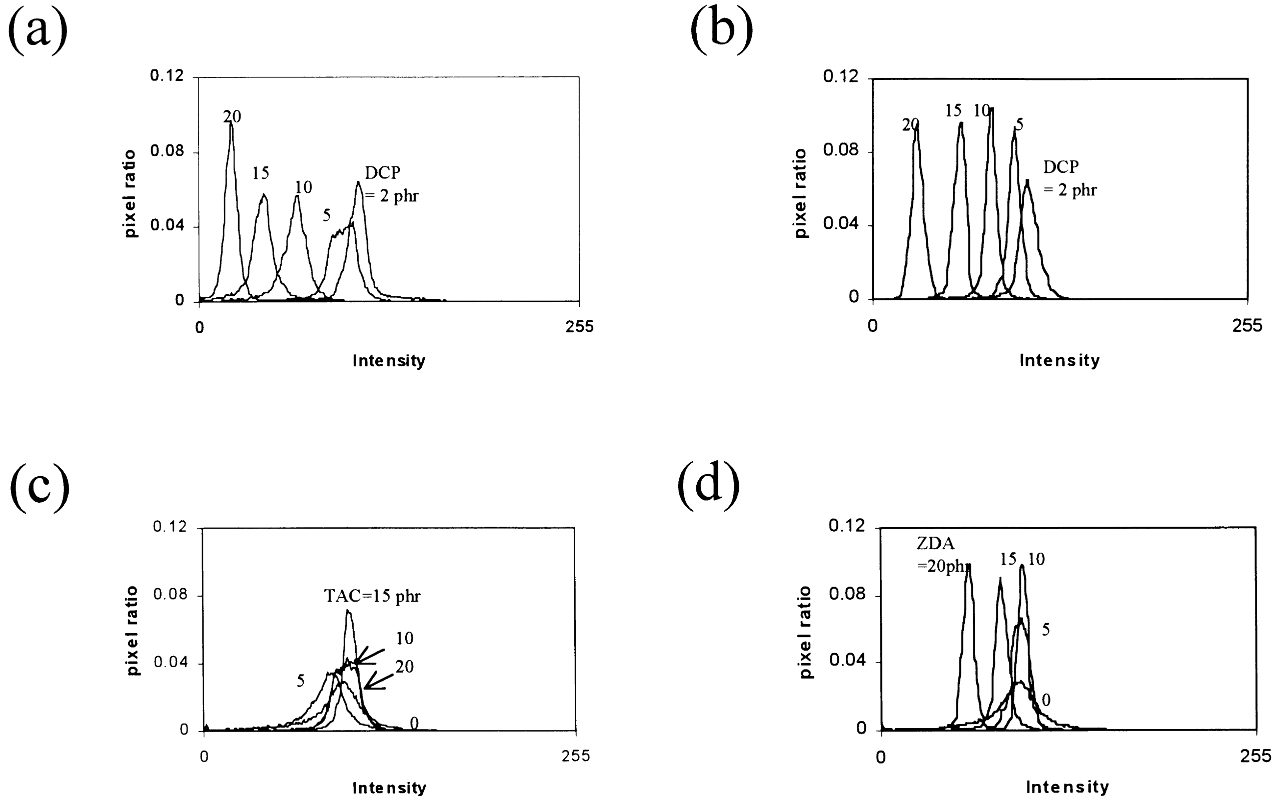

Fig. 5. Histograms of the images shown in Fig. 4. (a and b) variable peroxide concentration at 10 phr coagent (TAC (a), ZDA (b)) (c and d) variable coagent concentration at 5 phr DCP (TAC (c), ZDA (d)).

magnetic field. The result is an isotropic averaging of the chemical shifts for the solid similar to those observed in solution n.m.r. The three proton resonance peaks of *cis*-1,4-polyisoprene can be resolved under this condition. An olefinic proton peak at 5.2 ppm and two aliphatic proton peaks at 1.6 and 2.0 ppm are found. The spin–spin relaxation times, T_2, were calculated from the determination of the time constants of the decay curves, which were obtained by plotting the signal intensities as a function of echo time. It was known that the T_2 of elastomers can be resolved into short T_2 (T_{2S}) and long T_2 (T_{2L}) by using a biexponential model [25,26]. The short component is attributed to the rigid protons close to crosslinks and the long component is attributed to the mobile protons farther away from crosslinks. In this experiment, the long T_2 relaxation times (T_{2L}) were obtained from the decay curves, because the changes in mobile protons in the networks are more interesting. It was found that the olefinic protons and the aliphatic $-CH_3$ protons have similar T_{2L} values and the aliphatic $-CH_2-$ protons have the lower values. The difference in the T_{2L} relaxation times within the methylene protons is because of the difference in the mobility of the groups. Pendant $-CH_3$ groups have the higher T_{2L} relaxation times because of their free rotational motions, whereas the aliphatic protons in the *cis*- position have lower T_{2L} relaxation times due to their restricted bending motions. The proton T_{2L} relaxation times are dependent on the segmental mobility of the samples, which is sensitive to the crosslink density. The segmental mobility of the rubber matrix decreases with the addition of peroxide or coagent, therefore, decreases in the T_{2L} relaxation times are observed. The T_{2L} relaxation times of the peroxide/coagent systems are lower than the systems without the coagent, which suggests an increased crosslink density in the networks.

Solvent spin-echo images of the samples swollen in cyclohexane and the histograms of the images are shown in Figs. 4 and 5. The pixel ratios were calculated by dividing the pixel numbers at a certain intensity by the total number of pixels in the image. Samples of different crosslink densities can be obtained by varying the peroxide concentration. Less solvent is imbibed into samples with higher crosslink densities and this results in decreases in image intensity. (Fig.4(a) and 5(a) and (b)) Heterogeneity is found in those images with low voxel intensity, which can be highly crosslinked regions or coagent domains. The heterogeneity can also be confirmed by monitoring the broadness of the histogram profile. The heterogeneity is more notable in the case of the TAC coagent system than the ZDA coagent system, which could be related to the physical properties of the coagents. TAC coagent is a liquid and ZDA is a solid at the crosslinking temperature. The TAC at the crosslinking temperature has enough mobility to form domains, therefore, its use results in more heterogeneous structures. Solvent spin-echo images of different coagent

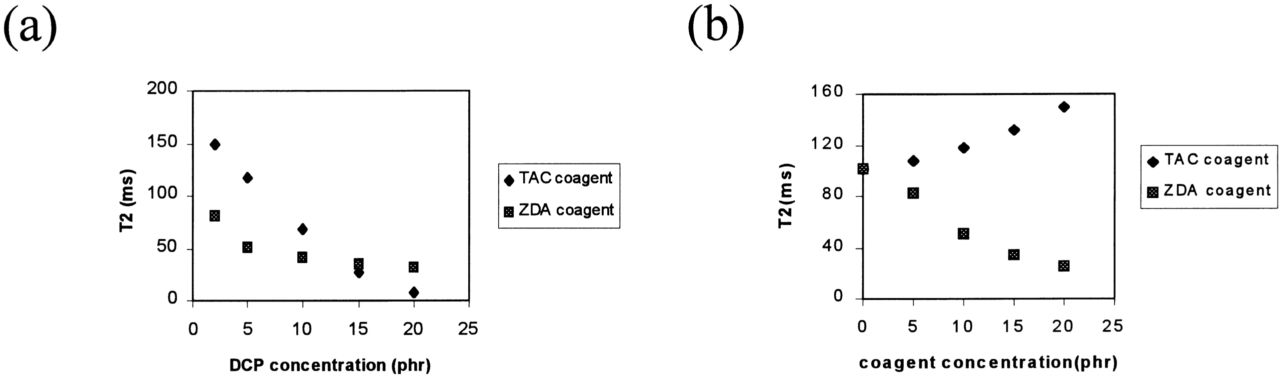

Fig. 6. The solvent proton T_2 relaxation times of peroxide/coagent crosslinked samples swollen in cyclohexane: (a) peroxide concentration variation at coagent, 10 phr and (b) coagent concentration variation at DCP, 5 phr. The experiments were performed with CP/MAS probe without the sample spinning.

concentrations are shown in Fig. 4(b) and the histograms are also shown in Fig. 5(c) and (d). In the TAC system, there are no significant changes in the image intensities although there is a swelling ratio decrease with increasing coagent concentration. (Fig. 2(b)) This is because the n.m.r. images are dependent on spin density as well as the T_2 relaxation time of the protic solvent [13]. The T_2 relaxation times measured with a CP/MAS probe explain the results. Fig. 6(b) shows the increase in T_2 values with the increase in the TAC coagent concentration. The combination of the two effects of spin density and T_2 relaxation time possibly results in no change in the image intensities in the TAC system. However, decreases in the image intensities were observed with an increase in the ZDA concentration because both the spin density and the T_2 relaxation time of the solvent decrease.

It is known that the motion of the solvent in the polymer solution such as self-diffusion is reduced by an obstruction effect [27,28], which increases with a decrease in free volume. The motion is also influenced by the attractive or the bonding interactions with the polymer [29]. T_2 relaxation times of the swelling solvent decrease with an increase in the peroxide concentration. (Fig. 6(a)) The cyclohexane imbibed into the highly crosslinked networks with reduced free volumes shows the restricted molecular motions, so that it exhibits the decreased T_2 relaxation times. Different behaviors were observed with the change in the coagent concentration. (Fig. 6(b)) T_2 relaxation times of cyclohexane increase with TAC coagent and decrease with ZDA coagent. The solvent-polymer interaction is thought to play a role in the solvent T_2 increase in the TAC coagent system. The decrease in the polymer-solvent interaction by copolymerization of molecules may result in the increase in T_2 relaxation times. The ZDA system does not show the same trend, because it exists as phase-separated solid domains.

Solvent spin-echo T_2 images of crosslinked samples swollen in cyclohexane were generated from four images with different spin-echo times. (Fig. 7) The average T_2 values

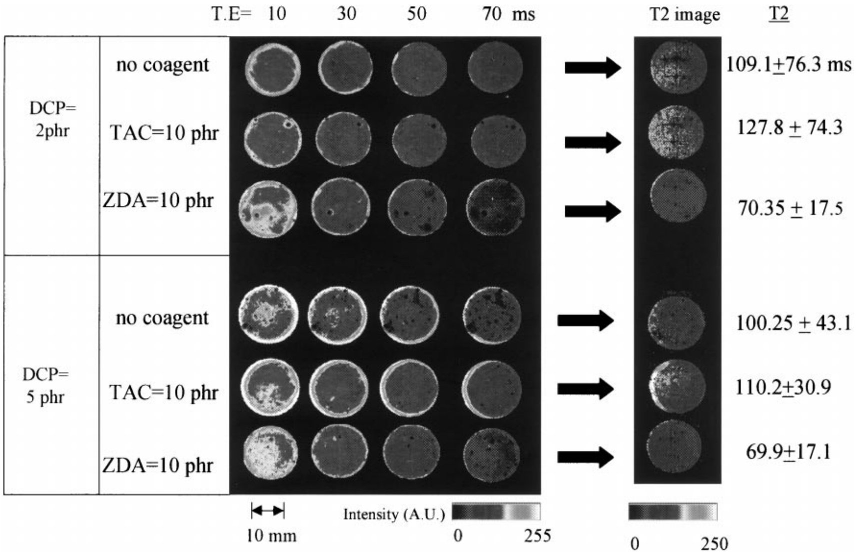

Fig. 7. The solvent spin-echo images of the crosslinked samples swollen in cyclohexane. The T_2 images were computer-generated from the different spin-echo time images.

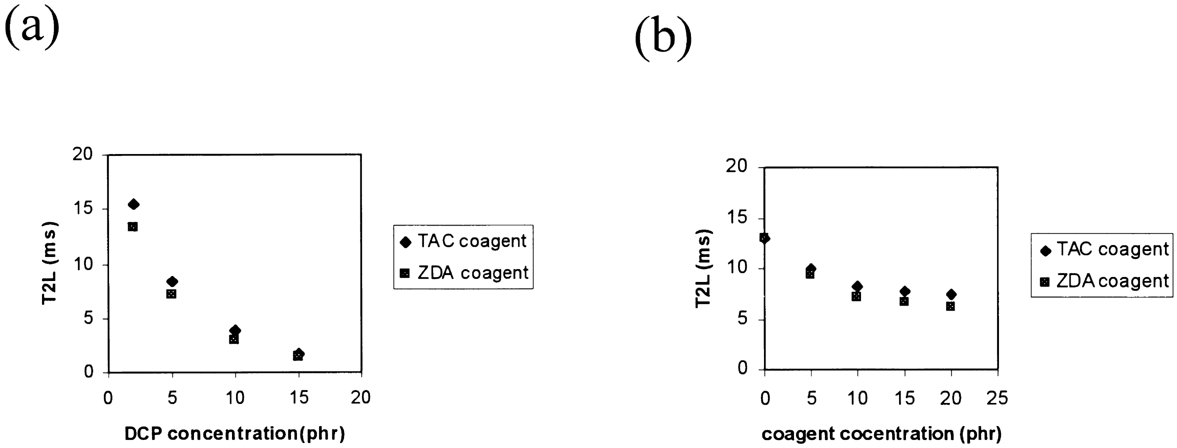

Fig. 8. The proton T_{2L} relaxation times of the peroxide/coagent crosslinked samples at 1.6 ppm: (a) peroxide concentration variation at 10 phr coagent and (b) coagent concentration variation at 5 phr DCP. The experiments were performed with CP/MAS probe and CPMG pulse sequences at the spinning rate of 3.5 kHz.

obtained from the T_2 images are shown together. It is also observed that there is a decrease in the T_2 relaxation time of cyclohexane with the increase in peroxide concentration. There is a slight increase in the T_2 relaxation time with the TAC coagent addition, which is in good agreement with the T_2 measurements acquired with the CP/MAS probe. (Fig. 6(b)) The ZDA coagent system shows the decrease in T_2 relaxation times in the images, which is due to increased crosslinks from coagent-rubber reactions.

The changes in the proton relaxation times (T_{2L}) of the TAC system at 1.6 ppm are compared to the ZDA system in Fig. 8. The increase in the peroxide and the coagent concentrations results in decreases in T_2 relaxation times. The ZDA system shows lower T_{2L} values compared to the TAC system. The relative immobility of ZDA may cause such a difference. The same trend can also be observed from the different echo time experiments with n.m.r. imaging. The samples are swollen in a deuterated solvent to increase the S/N ratio of the rubber proton spin-echo signals. From the images acquired with different spin-echo times, T_2 images of rubber protons can be generated.

4. Conclusions

It was observed that the long T_2 relaxation times of rubber protons in peroxide/coagent crosslinked elastomer decrease with the increase in the crosslink density resulting from the addition of peroxide or coagent. The T_2 relaxation times of a protic solvent in the swollen networks are affected by the physical property changes in the networks. It was concluded that the solvent T_2 relaxation times depend on solvent-polymer interactions as well as the crosslink density of the networks.

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