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# Solid-state NMR study of natural rubber blended with EVA and EVA modified with mercaptoacetic acid

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## Abstract

Solid-state $^{13}C$ NMR spectroscopy involving magic angle spinning (MAS) techniques with and without cross-polarization was employed for interaction studies in natural rubber (NR)/EVA and NR/mercapto-modified EVA (EVASH) blends. From arrayed of variable contact time spectra, the proton $T_1\rho$ values were determined at short contact times to analyze the EVA or EVASH domains and longer contact times to investigate the interactions in the NR domains. Substantial changes have been observed when dicumyl peroxide was employed as curing agent in NR/EVASH and NR/EVA/EVASH blends.

## Introduction

It is well known that nuclear relaxation has been used to get information on polymer-polymer compatibility.[1-5] Such informations can be derived from solid state $^{13}C$ NMR studies of polymer blends involving magic angle spinning (MAS) with cross-polarization (where the intensity of peaks in the $^{13}C$ NMR spectrum will vary depending on the participation of the relevant molecular fragment in the different domains, and on the relationship of the variables such as, contact time and recycle time) and without cross-polarization (the omission of the cross-polarization (CP) technique leads to spectra depending on $T_1C$ and recycle time). [1,9] The combined techniques of CP/magic-angle spinning (MAS)/high power proton decoupling (HPHD) are the standards to obtain high-resolution liquidlike spectra in the solid-state. These combined techniques together with the variation contact time and MAS experiments are able to describe the molecular mobility of polymeric materials as well as to provide information on sample homogeneity.

Recently, the compatibilization of natural rubber (NR)/EVA blends has been studied by employing mercapto-modified EVA (EVASH). [10-11] It was suggested that NR can chemically interact with EVASH through the mercapto groups, giving rise to a grafted or crosslinked system. These interactions are improved by the presence of dicumyl peroxide (DCP) as the curing agent.[11]

In this communication, we investigate the interactions between NR and EVASH and the effect of DCP on these interactions by using the solid-state NMR techniques described above.

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## Experimental

**Materials and blend preparation.** Natural rubber (NR) (Malaysia) (specific gravity 0.93 g/cm$^3$) and poly(ethylene-co-vinyl acetate) (EVA) (Triunfo, RS, Brazil) (vinyl acetate content = 18wt%, melt flow index = 2.3 g/10min) were used without purification. SH-modified EVA was prepared by esterification of hydrolyzed EVA with 2-mercaptoacetic acid, according to the literature procedure. [12-13] The corresponding poly((ethylene-co-mercaptovinyl acetate) (EVASH) contains 195.82 mmol SH/100g.[10]

Blends were prepared in a Berstoff two roll-mill at 130°C and 30 rpm for 5 min and compression molded at 13.8 MPa and 150°C for 5 minutes..[10]

**NMR measurements.** All NMR spectra were obtained on a Varian VXR 300 spectrometer operating at 299.9 MHz and 75.4 MHz for $^1$H and $^{13}$C, respectively. All experiments were done at ambient probe temperature and with high power decoupling. Zirconium oxide rotor of 7mm diameter with Kel-F caps was used to acquire the NMR spectra at rates of c.4KHz. $^{13}$C spectra are referred to the chemical shift of the methyl group carbons of hexamethylbenzene (17.3ppm). The $^{13}$C were carried out in the cross-polarization mode with magic-angle spinning; variation contact time and magic-angle spinning (MAS). A range of CP contact was established as 200 μs to 12000 μs for the samples. Proton $T_1{}^H\rho$ were determined from the intensity attenuation of carbon-13 peaks with increasing contact times.

## Results and discussion

The study of polymer blends mobility is possible by comparing proton-decoupled $^{13}$C NMR spectra obtained under CP/MAS and MAS conditions. The MAS spectra were obtained at very short recycle time, so that only the mobile domain or amorphous phase can be detected. CP/MAS spectra must be recorded under the optimum contact time to be representative of the whole sample, since under such circumstances the behavior of the $^{13}$C spins depends on proton relaxation characteristics. Fig. 1 shows the solid-state $^{13}$C NMR spectra of NR using the CP/HPHD/MAS (a) and MAS/HPHD (b) techniques. No appreciable changes in both spectra were detected, which can be a first indication of the presence of one domain with high molecular mobility, as a consequence of absence of crystallinity.

The CP/MAS spectra of EVA and EVASH present a single peak at $\delta$ = 33.2ppm related to -CH$_2$- groups. In both cases, a small displacement of this peak toward $\delta$ = 31.2ppm was observed when the spectra were recorded under MAS condition. This behavior is normally attributed to differences in molecular motion as a result of regions of different conformations and indicate the presence of amorphous and crystalline phases.

The signal form distribution of an arrayed set of variable contact spectra may give useful information on chain flexibility. It is known that rigid samples take shorter time to cross-polarize, while mobile samples need longer time to be polarized. Fig. 2 exhibits an arrayed set of CP/MAS spectra for NR. As expected, the form of distribution is displaced to the flexible region, which is in agreement with the behavior of flexible sample. The arrayed set of CP/MAS spectra for NR/EVA (80:20 phr) or NR/EVASH (100:5 phr) suggests two domains without interactions between them; one is related to EVA or EVASH and the other is related to the NR phase.

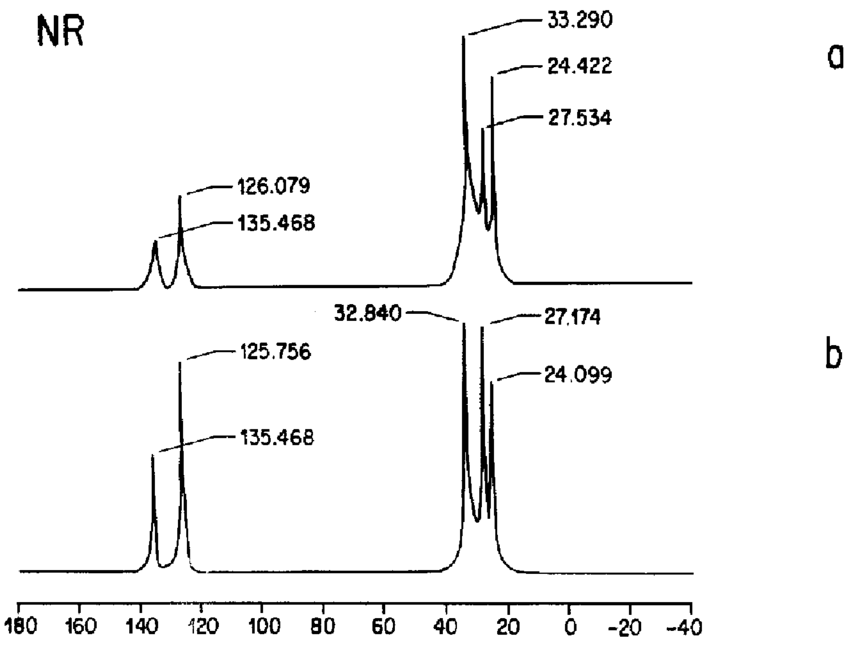

**Fig. 1.** Solid-state $^{13}C$ NMR spectra of NR using the CP/HPHD/MAS (a) and MAS/HPHD (b) techniques.

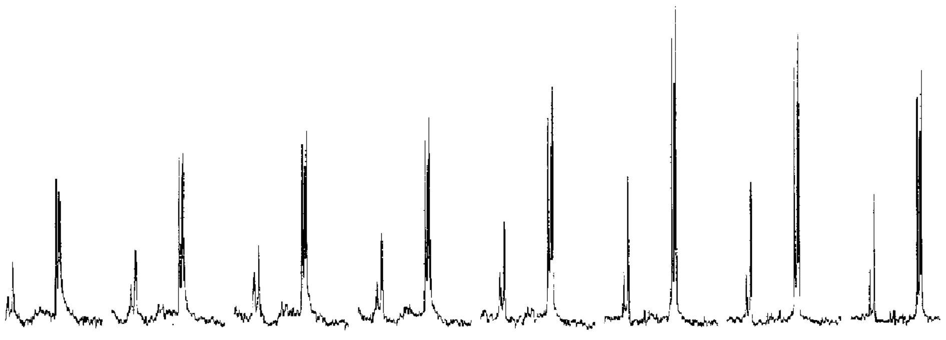

**Fig. 2.** Arrayed set of carbon-13 CP/MAS spectra of NR.

The addition of 0.7 phr of DCP to the NR/EVASH (100:5 phr) system promotes good interaction among all blend components. Indeed, the results of variable contact time, shown in Fig. 3, also suggest the presence of two domains, but, signals corresponding to both polymers are observed in these domains. Similar behavior has been detected in the NR/EVA/EVASH (80:20:5phr) system with 0.7 phr of DCP.

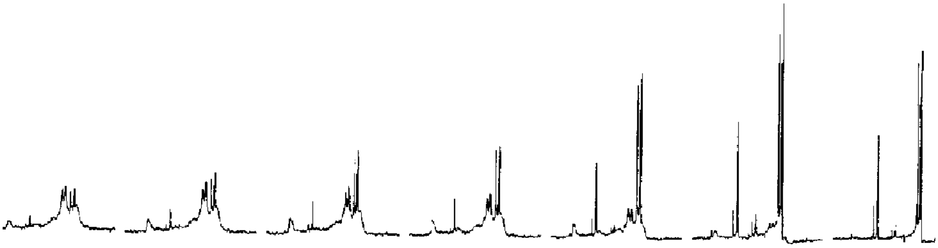

**Fig. 3.** Arrayed set of carbon-13 CP/MAS spectra of NR/EVASH/DCP (100:5:0.7 phr)

Arrayed of variable contact time spectra were analyzed to obtain the $T_1\rho$ values according to the following equation[7]:

$$S(t) = \left[1 - e^{-t/T_{CP}}\right] e^{-t/T_1\rho}$$

which assumes that $T_{CP}$ is substantially less than $T_1\rho$. Table 1 presents $T_1\rho$ values taken from an arrayed of variable contact time from 200μs to 8ms. These proton $T_1\rho$ values correspond to the $CH_2$ signal ($\delta$=33.4ppm) related to EVA or EVASH, the more rigid component in the blends. It is well known that, for short contact times, signal intensity is determined by polarization dynamics. Therefore, the efficiency of cross-polarization is evident from the short values of $T_{CP}$, so that good sensitivity may be obtained in spite of the modest $T_1\rho$ values.

**Table 1**: Proton $T_1\rho$ of $CH_2$ signals (33.4 ppm) related to EVA or EVASH phase.

| Sample | $T_1H_\rho$ (ms) |
|---|---|
| EVA | 0.9 |
| NR/EVA(80:20 phr) | 0.8 |
| EVASH | 1.5 |
| NR/EVASH (100:5 phr) | 1.1 |

The results listed in Table 1 confirm the fact that the systems under investigation present at least two domains with different mobilities, since only signals of EVA or EVASH were detected in this range of contact time. The values of proton $T_1\rho$ of EVA do not present any sensible variations with the presence of NR, indicating that this system is incompatible. A small decrease in $T_1H_\rho$ related to EVASH was observed in the NR/EVASH blend but the difference is too small to indicate an influence of the NR phase.

Based on the proton relaxation parameter response, another range of contact-time was investigated (200-12000 μs) in order to measure the proton $T_1\rho$ values related to the NR phase in the blends. Table 2 shows the proton $T_1\rho$ data for the vinyl carbon (=$CH_2$) (δ=126.1ppm) and for the methylene carbon ($CH_2$) (δ=33.4ppm). Glass transition temperature of the NR phase are also presented.

The addition of EVA or EVASH results in a little increase in the $T_1\rho$ values of the vinyl carbon of the NR phase indicating an increasing of chain mobility of this phase. The presence of DCP reduces this chain mobility as indicated by the decreasing of $T_1\rho$ values. These results are in agreement with the Tg behavior of NR indicated in Table 2.[11] The proton $T_1\rho$ values for methylene carbon are more intriguing. NR/EVA or NR/EVASH blends do not display any significant change in this value. The addition of DCP to NR/EVASH blend causes a strong increase in $T_1\rho$ values. This behavior may be attributed to grafting of EVASH onto NR assisted by DCP. This grafting disturbs the arrangement of NR chains and contributes to better mobility. In previous work, it was observed that the addition of EVASH to NR results in a considerable decreasing of the n-heptane-extracted NR fraction as a consequence of the reaction between mercapto groups along the EVASH backbone and the NR phase.[10] It seems that the degree of the crosslinking is not high enough to be detected by $^{13}C$ NMR.

DCP is a well-known free radical generator and can abstract the hydrogen atom from mercapto groups in EVASH thus increasing grafting. The chain mobility of the NR phase strongly decreases in the NR/EVA (80:20phr) blend containing 5 phr of EVASH and 0.7 phr of DCP, as indicated by the lower $T_1\rho$ value for the methylene carbon when compared to the NR/EVASH/DCP system (see Table 2). DCP is a curing agent which may crosslink the NR and EVA phase.[14] These results suggest that DCP is acting not only as grafting accelerator of EVASH onto NR phase but also as a curing agent for both polymer phases, promoting a co-vulcanization between EVA and NR. This hypothesis is confirmed by previous results concerning the decrease in the degree of crystallinity of the EVA phase.[11]

**Table 2**: Proton $T_1\rho$ of NR signal in the samples.

| Sample | | Tg of NR phase, (°C) [11] | $T_1H_\rho$ (ms) | |
|---|---|---|---|---|
| | | | 126.1ppm | 33.4ppm |
| NR | | -56.9 | 10.4 | 11.8 |
| NR/EVA | (80:20phr) | -61.3 | 18.9 | 11.4 |
| NR/EVASH | (100:5phr) | | 18.9 | 12.7 |
| NR/EVASH/DCP | (100:5:0.7phr) | | 16.4 | 31.2 |
| NR/EVA/EVASH/DCP | (80:20:5:0.7phr) | -51.5 | 15.2 | 14.5 |

## Conclusions

As previously reported,[10] mercapto-modified EVA (EVASH) reacts with NR during melt processing. This interaction was suggested by experiments involving selective NR extraction with n-heptane. The extent of the graft reaction between EVASH and NR is insufficient to influence the mobility of both EVASH and NR domains and thus, no difference of $T_1H_\rho$ values corresponding to these components has been observed. The addition of DCP to the NR/EVASH system increases the graft reaction which affects the molecular mobility detected by NMR techniques. Such a blend presents also higher elongations as compared to pure NR or a NR/EVASH blend.[11] For NR/EVA/EVASH system, the presence of DCP decreases the molecular mobility as a consequence of the increase in the crosslinking degree. It is important to point out that DCP was added after all the other components have been blended. This procedure may affect the distribution of the curing agent into the polymeric phases. Because of its polar nature, DCP may have more affinity to EVA or EVASH. On the other hand, NR is easier to be crosslinked. This feature may promote a measure of co-vulcanization.

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