Imidazole-Accelerated Crosslinking of Epoxidized Natural Rubber by Dicarboxylic Acids: a Mechanistic Investigation by NMR Spectroscopy

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Electronic Supplementary Information

I. DSC experiments

II. NMR experiments

I. DSC experiments.

Experimental: NMR samples were analyzed by Differential Scanning Calorimetry (DSC), using a Q1000 series TA Instrument under nitrogen flow. Samples (5-10 mg) encapsulated in hermetic pans were submitted to a temperature ramp from -100 °C to +150 °C at a rate of 10 °C/min. To prepare homogeneous samples of DA+DMI, the two species were first mixed in a mortar and then heated at 70 °C until complete melting. The mixtures were then left at -4°C in order to let the salts of imidazole and carboxylic acid crystallize properly.

Results:

1. Solubility of the crosslinking agent before curing. Enthalpies of melting of pure DA (Fig. S1-A, $\Delta H = 230 \text{ J/g}$) and DA dispersed in the rubber (Fig. S1-B, $\Delta H = 95 (\pm 15) \text{ J/g}$) may be compared to estimate the solubility of the diacid in the rubber. The ENR/DA mixture containing 43 wt% of DA, it follows that about 95 % of DA is crystallized in the matrix. When comparing pure salt (Fig. S2-A, $\Delta H = 135 \text{ J/g}$) and salt dispersed in the matrix (Fig. S2-B, $\Delta H = 35 (\pm 5) \text{ J/g}$), and considering that the ENR/DA/DMI mixture contains 58 wt% of salt, it may be deduced that only 45 % of the salt may be crystallized in the rubber. The salt is thus much more soluble than DA in the ENR50 matrix.

2. Compared thermograms after curing. After curing for 3 hours at 180 °C without DMI, a melting peak that could correspond to remaining DA is still present (Fig. S1-C). By contrast, no trace of residual salt is observed in the sample cured for 20 min in presence of DMI (Fig. S2-C). This observation is in accordance with the NMR results.



Figure S1: DSC traces of (**A**) pure DA, (**B**) ENR/DA blends before curing, (**C**) ENR/DA blends after curing for 3 hours at 180 °C.



Figure S2: DSC traces of (A) pure DA/DMI salt, (B) ENR/DA/DMI blends before curing,(C) ENR/DA/DMI blends after curing for 20 minutes at 180 °C.

II. NMR experiments.

Experimental: The solid-state NMR experiments were performed on as-prepared materials (regular disks stacked within the rotor) and were not cryo-grinded. Thus, while a stable rotation was obtained up to 10 kHz, weak coil vibrations systematically occurred above 8 kHz. The ¹H NMR experiments were performed at 10 kHz in order to increase the spectral resolution: as the acquisition times were rather short, the risk of probe damages was quite limited. For the ¹³C NMR experiments that required longer experimental time, we decided to set the MAS spinning frequency at 5 kHz, to prevent any probe damage.

As the ¹³C NMR spectra were obtained well above the glass transition temperature of the ENR matrix, the spinning sideband intensities are rather weak and can sometimes hardly be observed, even for the ENR olefinic carbons. More intense spinning sidebands are observed for the ester carbons of the diacid under its crystalline form since no (or nearly no) motions occur within the crystallites. However, at a MAS spinning frequency of 5 kHz, these spinning sidebands do not suffer from any overlap with any other resonance and such a MAS frequency thus appears as a good compromise value.

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Additional NMR spectra: Comparison of the following spectra indicate a solubilisation of DA in presence of DMI, corresponding to the formation of an imidazolium dicarboxylate salt.



Figure S3: ${}^{1}\text{H} \rightarrow {}^{13}\text{C}$ CP/MAS/DD NMR spectra recorded at 60 °C before curing, on (A) ENR/DA/DMI blends, (B) ENR/DA blends (i.e. as Fig. 2A). For these experiments, the contact time t_{CP} was set to 1 ms.