1. Experimental Section

Materials. Epoxidized natural rubber (ENR) with an epoxidization degree of 50% was kindly provided by the Agricultural Products Processing Research Institute, Chinese Academy of Tropical Agricultural Science, China. Sebacic acid (SA, 99%), 1,2-dimethylimidazole (DMI, 99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), and N-acetylglucose (NAg, 98%) were purchased from Sigma-Aldrich. All the chemicals are used as received.

Sample preparation. Desired amounts of SA, NAg, DMI, and TBD were successively compounded with ENR on a two-roll mill for about 15 min, following by compression at 180 °C for the optimum curing time determined by a vulcameter. The stoichiometry of epoxy groups from ENR and carboxyl groups from SA was fixed at 35 in all the
formulations. The content of NAg was controlled to be 0, 2, 4, 6, 8 wt% relative to ENR. The quantity of DMI and TBD were 70 mol% and 20 mol% relative to the carboxyl groups of the incorporated SA, respectively. DMI acts as accelerator to promote the esterification reaction between epoxy and carboxyl groups, and TBD acts as catalyst to accelerate transesterification reaction. In the context, sample code of ENR-\textit{x}N refers to crosslinked ENR with \textit{x} wt% of NAg.

**Characterizations.** Curing kinetics were determined at 180 °C using a U-CAN UR-2030 vulcameter. Fourier transform infrared spectroscopy (FTIR) was collected on a Bruker Vertex 70 FTIR spectrometer equipped with a heating cell, and all the spectra were normalized by using the absorption intensity of –CH\textsubscript{3} at 2963 cm\textsuperscript{-1} as an internal reference.

Tensile tests were performed on dogbone-shaped samples (ca. 60 mm × 4 mm × 1 mm and a gauge length of 35 mm) using a U-CAN UT-2060 instrument at room temperature. For uniaxial tensile tests of ENR-\textit{x}N, the extension rate was 500 mm/min. Five specimens were measured for each sample, and the average value was calculated. For cyclic tensile tests, both loading and unloading were conducted with an extension rate of 500 mm/min at a predefined strain of 200%.

Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments DSC Q10 by heating under a nitrogen purging. Each sample around 8-10 mg in a standard DSC pan was maintained at 60 °C for 2 min to eliminate heat history. The sample was cooled down to –40 °C and then heated to 60 °C at 10 °C /min.

Creep experiments and stress relaxation experiments were performed on a rectangular specimen (10 mm × 4 mm × 0.5 mm) by using a TAQ800 DMA apparatus.
For creep experiments, a nominal stress of 0.1 MPa was applied on the sample after a
30 min temperature equilibration. For stress relaxation tests, the sample was initially
preloaded with $1 \times 10^{-3}$ N force to maintain straightness and equilibrated for 30 min at
the required temperature. The sample was then stretched to a constant strain of 2%, and
the stress decay was monitored over time.

Recycling of the rubbers was conducted by cutting the specimens into small chips
and compression molding under 10 MPa at 180 °C for 5 min.

Cross-linking density was determined by equilibrium swelling experiment based on
Flory-Rehner equation. Equilibrium swelling experiments were conducted by
immersing samples in toluene at room temperature for 72 h. After swelling, the solvent
was wiped off quickly from sample surface using filter paper, and the samples were
immediately weighed and then dried in a vacuum oven at 60 °C until constant weight.
Three specimens were measured for each sample.

The volume fraction of ENR in the swollen sample, $V_r$, was calculated by the
following equation:

$$V_r = \frac{(m_2 - m_0 \phi)/\rho_r}{(m_2 - m_0 \phi)/\rho_r + (m_1 - m_2)/\rho_s}$$

(1)

where $m_0$ is the sample mass before swelling, $m_1$ and $m_2$ are the weights of the swollen
and deswollen sample, respectively; $\phi$ is the weight fraction of the insoluble
components, $\rho_r$ and $\rho_s$ are the densities of the rubber and solvent, respectively.

The elastically active network chain density can be calculated by the well-known
Flory-Rehner equation:
\[ V_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - V_r/2)} \]  

(2)

where \( \chi \) is the Flory-Huggins polymer solvent interaction parameter (0.341 for ENR and toluene), and \( V_s \) is the molar volume of the solvent (106.5 cm\(^3\)·mol\(^{-1}\) for toluene).

2. Additional Experimental Data

Table S1. Cross-linking density and detailed mechanical properties of ENR-xN.

| Samples   | Cross-linking density (10\(^{-4}\) mol/cm\(^3\)) | Stress at 300\% strain (MPa) | Tensile strength (MPa) | Breaking strain (%) | Fracture energy (MJ/m\(^3\)) |
|-----------|-----------------------------------------------|-----------------------------|-----------------------|---------------------|-----------------------------|
| ENR-0N    | 5.91±0.05                                     | 2.35±0.04                   | 5.62±1.14             | 460±32              | 10.0±0.5                    |
| ENR-2N    | 7.12±0.02                                     | 2.66±0.13                   | 10.11±0.22            | 526±8               | 15.7±0.2                    |
| ENR-4N    | 8.63±0.13                                     | 3.00±0.10                   | 12.90±0.07            | 516±3               | 17.8±1.0                    |
| ENR-6N    | 11.37±0.07                                    | 4.12±0.39                   | 18.15±1.66            | 490±15              | 23.8±1.2                    |
| ENR-8N    | 13.29±0.47                                    | 7.09±0.49                   | 27.97±1.22            | 493±11              | 40.2±1.4                    |

To clearly verify the role of DMI and TBD, two sets of control samples (ENR-0N without DMI and ENR-0N without TBD) were prepared. The cross-linking process was monitored by measuring the torque value at 180 °C on a rheometer. As shown in Figure S1, ENR-0N and ENR-0N without TBD exhibit similar curing profiles, and the torque values increase with time and then level off after 30 min, indicating that the cross-linking reaction is complete. However, ENR-0N without DMI exhibits a long marching curing process. These observations suggest that DMI play a critical role in accelerating the chemical reaction between epoxy and carboxyl groups.
Figure S1. Cross-linking kinetics of ENR-0N, ENR-0N without DMI and ENR-0N without TBD.

Figure S2. (a) Comparison on the FTIR spectra for uncured and cured ENR-0N. (b) FTIR for ENR-0N and ENR-6N. The spectra are normalized by using the absorption intensity of –CH$_3$ at 2963 cm$^{-1}$ as an internal reference.
Figure S3. DSC thermograms for ENR-\(x\)N.

Figure S4. (a) Loading-unloading cycles of ENR-0N. (b) Hysteresis energy of ENR-\(x\)N as a function of NAg loading.
Figure S5. Time dependence of $f^*(t)$ under uniaxial deformation for ENR-6N at various strain rates.

Figure S6. Stress relaxation for ENR-xN at 180 °C with a 2% strain.
Figure S7. Stress relaxation curves for ENR-0N, ENR-6N, ENR-H at 160 °C with 2% strain.

Figure S8. Stress relaxation curves for ENR-0N and ENR-0N/Ne (by adding equal molar number of N-ethylacetamide as that of NAg in ENR-6N into ENR-0N) at 160 °C with 2% strain.
Figure S9. Stress relaxation curves for (a) ENR-0N, (b) ENR-2N, (c) ENR-4N and (d) ENR-8N at different temperatures with a constant strain of 2%.

Figure S10. Fitting of $\tau^*$ to the Arrhenius equation for ENR-$x$N.

Characteristic relaxation times ($\tau^*$) follow an Arrhenius law with the temperature $\tau(T) = \tau_0 \exp (E_a/RT)$, where $\tau_0$ is the characteristic relaxation time at infinite time, $E_a$ is the
activation energy for the transesterification reactions, R is the universal gas constant and T is the temperature at the experiment conducted.

**Figure S11.** Stress-strain curves of recycled (a) ENR-0N, (b) ENR-2N, (c) ENR-4N (d) ENR-6N and (e) ENR-8N.
**Figure S12.** FTIR spectra of ENR-6N before and after reprocessing. The spectra are normalized by using the absorption intensity of –CH$_3$ at 2963 cm$^{-1}$ as an internal reference.

**Figure S13.** The cross-linking density of original and recycled ENR-xN.

**Reference**

1. Flory, P. J., Statistical Mechanics of Swelling of Network Structures. *J Chem. Phys.* **1950**, *18* (1), 108-111.