Electronic Supplementary Information (ESI)

Facile Strategy to Incorporate Amidoxime Groups into Elastomers toward Self-Crosslinking and Self-Reinforcement

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Equilibrium swelling experiments.

Total crosslinking density was determined by equilibrium swelling experiments. The vulcanizates were immersed in toluene at room temperature for 72 h. Then, the samples were removed from the solvent, and immediately weighed after wiping off the surface residual toluene, and then dried in a vacuum oven at 60 °C until a constant weight. The sol fraction is calculated according to $(m_0 - m_2)/m_0$, and the swelling ratio is defined as $(m_1 - m_2)/m_2$, where m_0 is the weight of the sample before swelling, and m_1 and m_2 are the sample masses before and after drying, respectively. The crosslinking density was determined by the classical Flory−Rehner equation.

$$V_e = -\frac{\ln\left(1 - V_r\right) + V_r + \chi V_r^2}{\mathrm{V_s}\left(V_r^{\frac{1}{3}} - \frac{V_r}{2}\right)}$$

V_r is the volume fraction of rubber in the swollen gel, V_s is the molar volume of the solvent (106.5 cm^3/mol for toluene), and χ is the Flory-Huggins solvent-polymer interaction parameter and is calculated as below:

$$\chi = 0.487 + 0.228 * V_r$$

V_r was calculated according to the equation below:

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

φ is the weight fraction of the insoluble components (in this system it should be considered as 0), and ρ_r and ρ_s are the density of rubber and solvent, respectively.

Covalent crosslinking density was determined by equilibrium swelling experiments as well. The vulcanizates were immersed in dichloroacetic acid/toluene solution (volume ratio 1:4) at room temperature for 72 h (replace the solution every 24 hours).[1] The subsequent processing and calculation methods are consistent with total crosslinking density.

Table S1. Mechanical properties of virgin NBR and AO-NBR

Samples	Stress at 100% (MPa)	Stress at 300% (MPa)	Tensile Stress (MPa)	Elongation at break (%)
Virgin NBR	0.5	0.4	0.5	1825
AO-NBR-2	0.7	0.7	1.6	1818
AO-NBR-5	0.9	1.0	2.5	1152
AO-NBR-10	1.3	2.1	5.3	650
AO-NBR-15	1.3	2.4	5.6	608

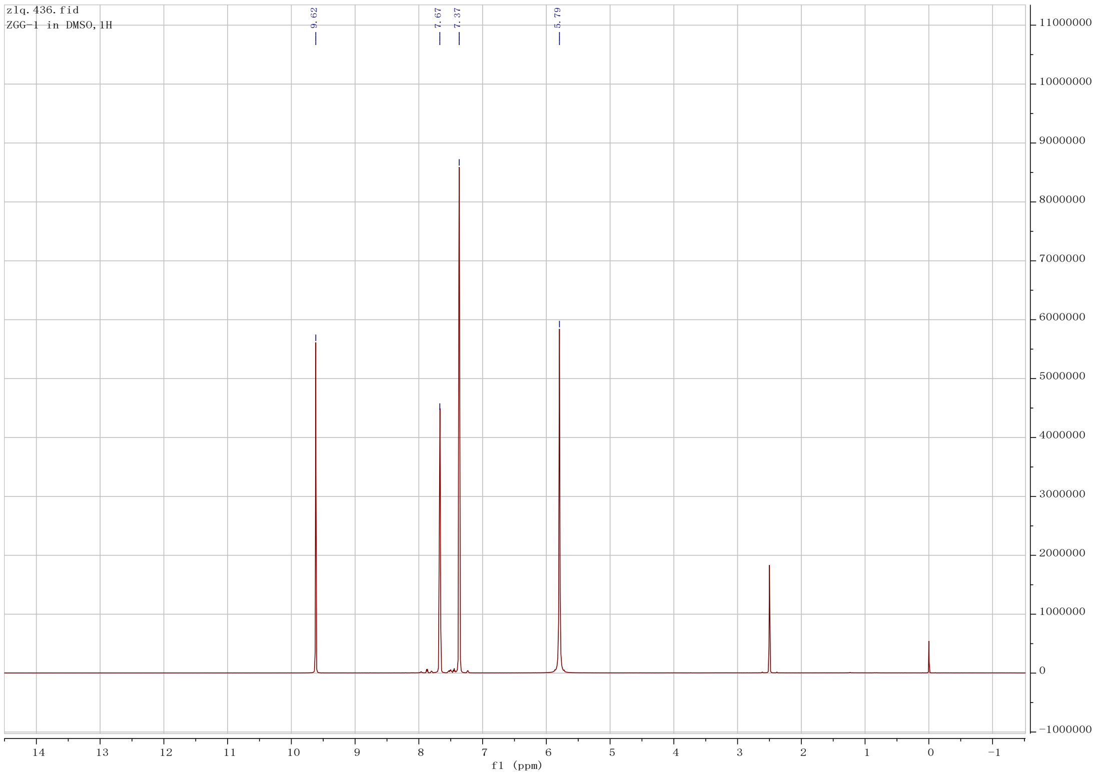


Fig S1. ^{1}H NMR spectrum of BAO.

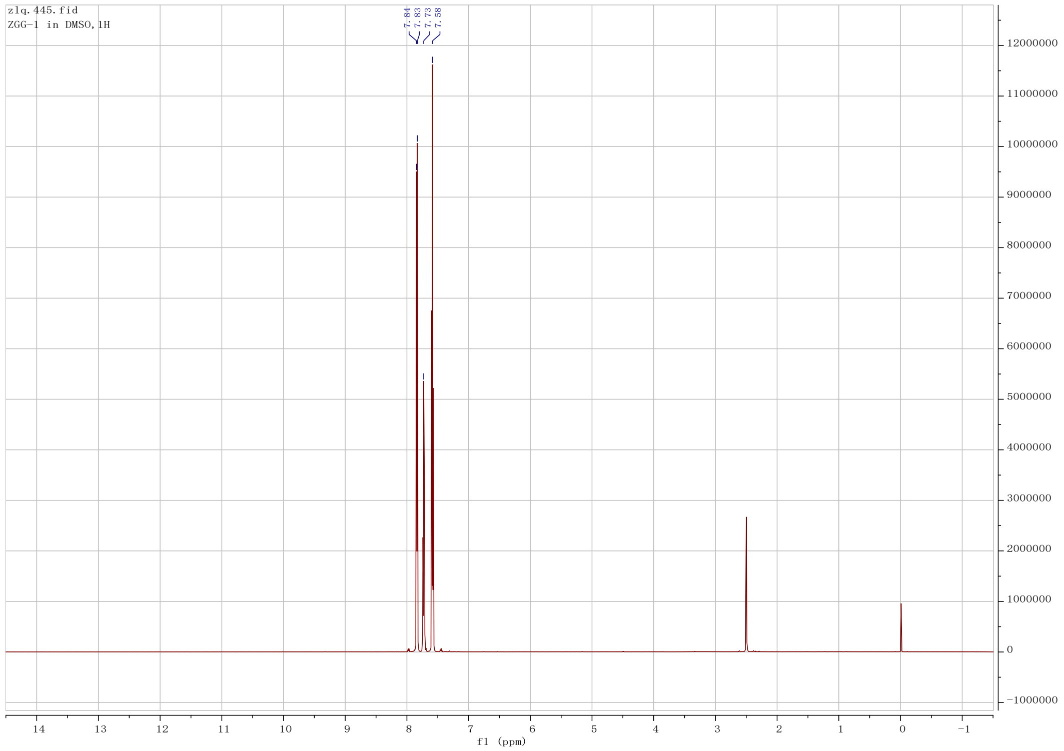


Fig S2.^{1}H NMR spectrum of BN

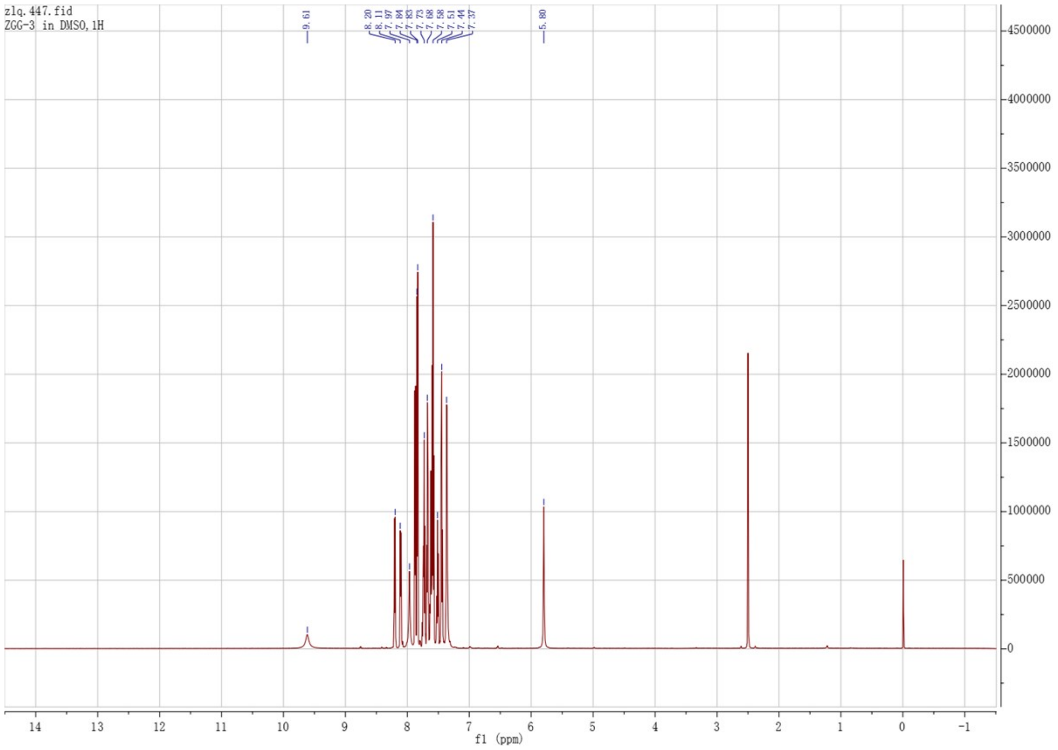


Fig S3.^{1}H NMR spectrum of the mixture of BAO and BN at 160 ℃ for 2 h.

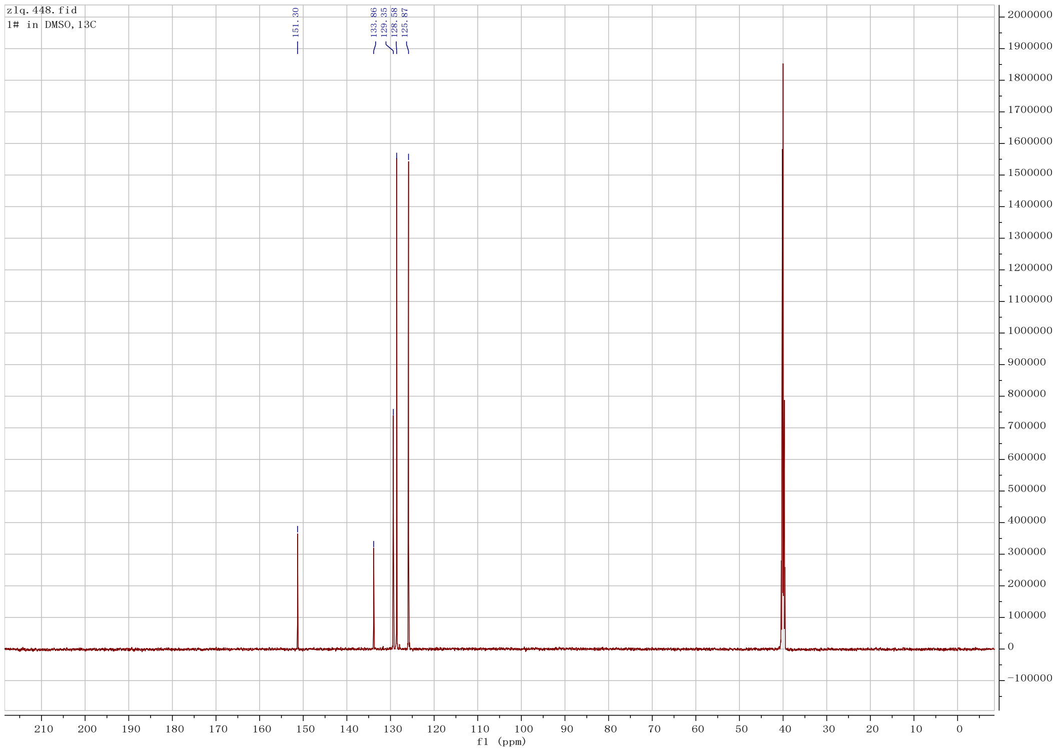


Fig S4.^{13}C NMR spectrum of BAO.

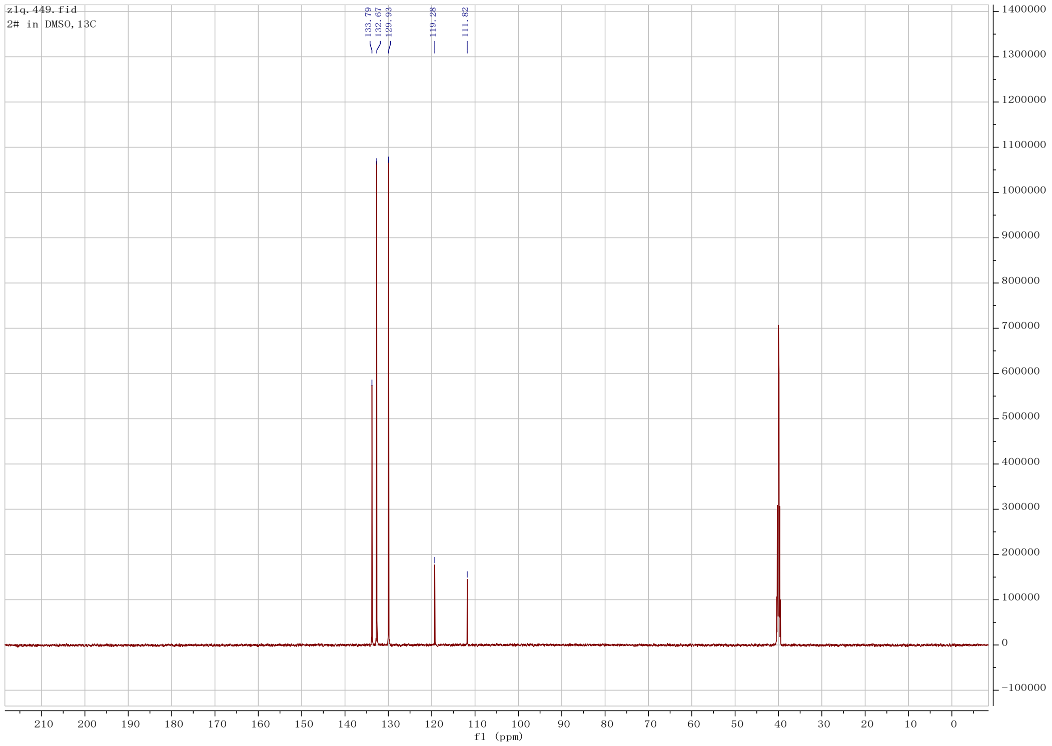


Fig S5.^{13}C NMR spectrum of BN

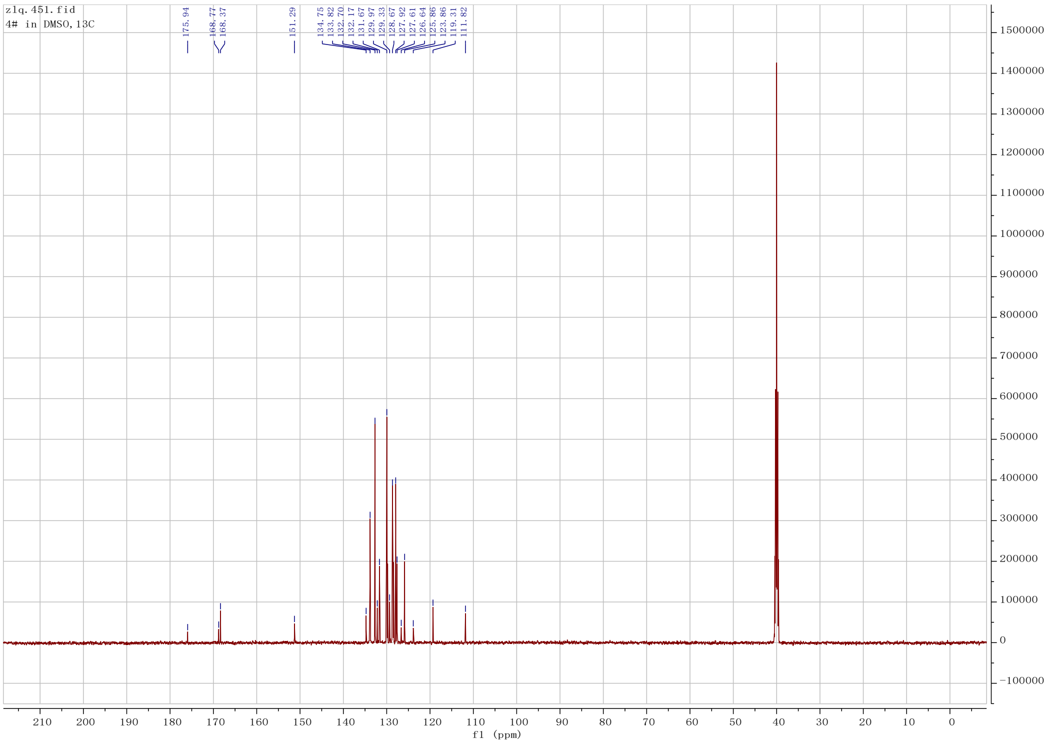


Fig S6.^{13}C NMR spectrum of the mixture of BAO and BN at 160 °C for 2 h.

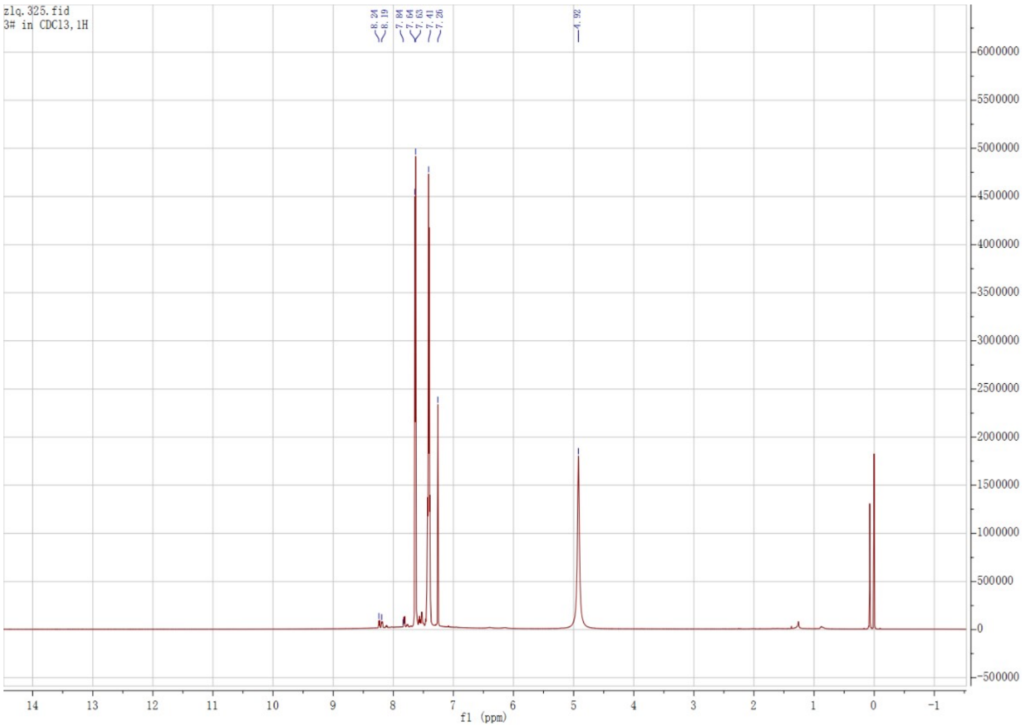


Fig S7.^{1}H NMR spectrum of BAO at 160 °C for 2 h.

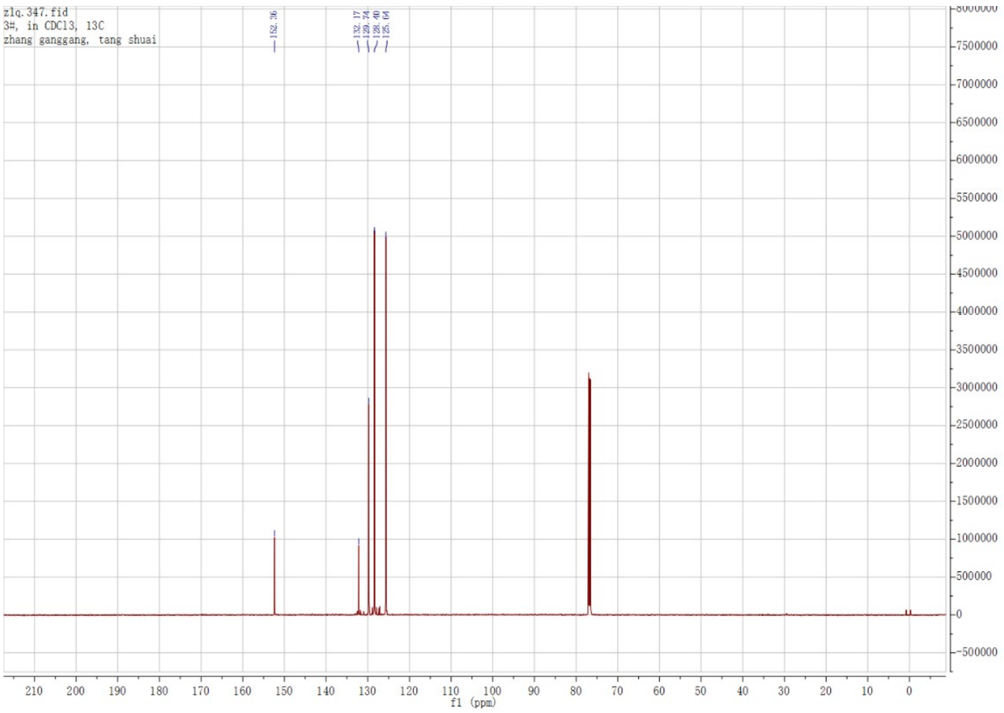


Fig S8.^{13}C NMR spectrum of BAO at 160 °C for 2 h.

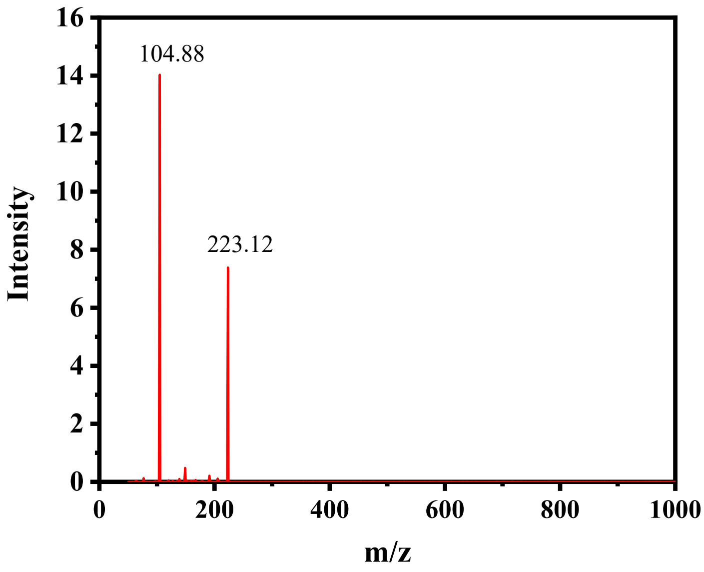
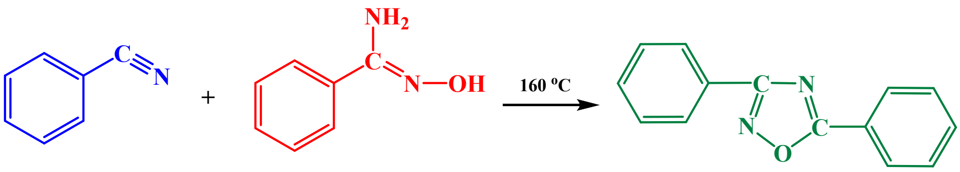


Fig S9. mass spectrum of the mixture of BAO and BN at 160 °C for 2 h



Scheme S1. Schematic illustration of the chemical reaction between BAO and BN.

Table S2. Mechanical properties of AO-NBR-*d* with different amidoxime concentration and molding time

Samples	Stress at 100% (MPa)	Stress at 300% (MPa)	Tensile Strength (MPa)	Elongation at break (%)
AO-NBR-5-*d*-30 min	1.9	5.4	5.9	326
D-AO-NBR-10-*d*-30 min	6.6	-	20.7	259
D-AO-NBR-15-*d*-30 min	14.4	-	16.8 (Yield)	133
D-AO-NBR-10-*d*-20 min	5.2	-	16.6	270
D-AO-NBR-10-*d*-40 min	8.7	-	16.4	173

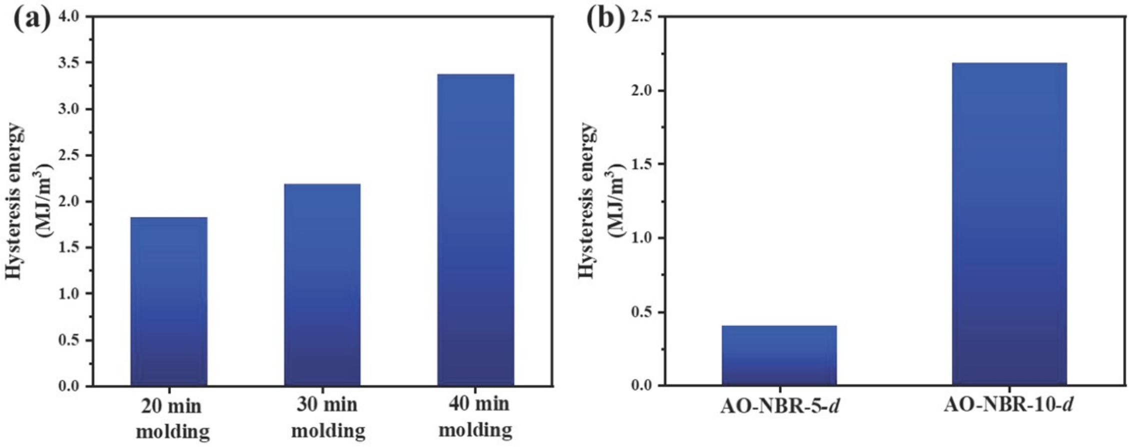


Fig. S10. Calculated hysteresis energy through first tensile cycle with AO-NBR-*d*, (a) with different molding time, (b) with various amidoxime concentration.

Table S3. Mechanical properties of T-AO-NBR nanocomposites with different amidoxime degree and $Zn(Ac)_2$ content

Sample	Stress at 100% (MPa)	Stress at 300% (MPa)	Tensile Stress (MPa)	Elongation at break (%)
AO-NBR-*t*-0.5 Zn	2.9	7.0	19.9	605
AO-NBR-*t*-1 Zn	3.1	8.6	25.2	579
AO-NBR-*t*-2 Zn	6.0	15.2	28.3	447
AO-NBR-5-*t*-Zn	3.2	8.8	12.4	408
AO-NBR-15-*t*-Zn	-	-	Yield (33.1)	70

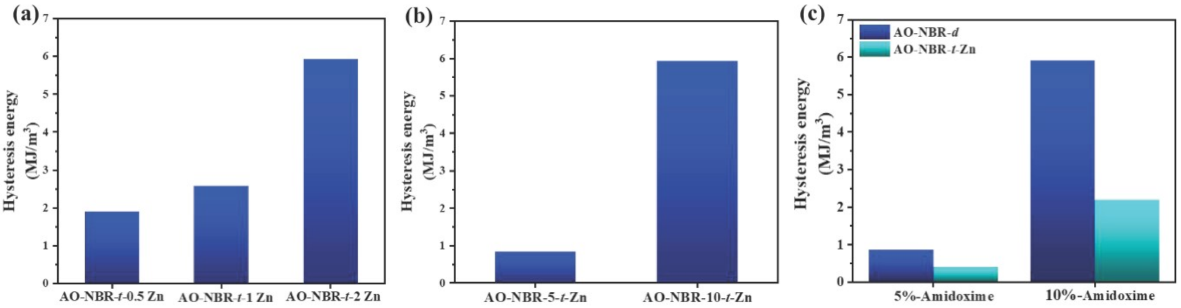


Fig. S11. Calculated hysteresis energy through first tensile cycle with AO-NBR-*t*-Zn (a) with different Zn contents, (b) with various amidoxime concentration; (c) Hysteresis energy comparison between AO-NBR-*d* and AO-NBR-*t*-Zn.

1. J. Liu, S. Wang, Z. Tang, J. Huang, B. Guo and G. Huang, *Macromolecules*, 2016, **49**, 8593-8604.