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Hybrid nitrile-based reactive diluent for phthalonitrile resins

Vladimir E. Terekhov, Oleg S. Morozov, Alexander V. Babkin, Alexey V. Kepman, Victor V. Avdeev and Boris A. Bulgakov

Materials and methods

All the manipulations with oxidation and moisture sensitive compounds were carried out under inert atmosphere using the standard Schlenk technique. Dimethylacetamide (DMAA) was purchased from Ekos-1 (Russia) and was used as received. 4-Nitrophthalonitrile was purchased from Central Drug House (India). Potassium carbonate was purchased from Soda Chlorate (Russia). Resorcinol was purchased from Zhejiang hongsheng chemical (China). 4-Nitrophthalonitrile, potassium carbonate and resorcinol were used as received. 4-Aminophenol and 4-cyanophenol were obtained from Acros Organics (USA) and used as received.

Nuclear magnetic resonance (NMR) studies were run on a Bruker Avance 600 at 600 MHz for ^{1}H and 151 MHz for ^{13}C with dimethyl sulfoxide-d_6 as solvent. Differential scanning calorimetry (DSC) was performed on a TA Instrument DSC Q20 at a heating rate of 10 K min^{-1} and an Ar purge rate of 100 ml min^{-1} and was applied for the determination of melting points of the monomers and the curing study. Thermal stability was evaluated by thermogravimetric analysis (TGA) on Netzsch TG 209 F3 Tarsus at a heating rate of 10 K min^{-1} in range 40–1000 °C and Ar or air purge rate of 250 ml min^{-1}. Glass transition temperature (T_g) was measured by the 3 point bending method on DMA Q800. Melt viscosity was measured with MCR 302 rheometer with cone 7 at 200 rpm. The coefficient of thermal expansion (CTE) was evaluated in the temperature range 20-250 °C on Netzsch TMA 402. Mechanical tests were carried out using Tinius Olsen H5K-S, Tinius Olsen 50ST, Tinius Olsen 300ST and Instron 5985 testing machines. The reported mechanical property values were based on an average of at least five tests.

Synthesis of 4-(4-cyanophenoxy)phthalonitrile (CPN)

4-Nitrophtalonitrile (346.1 g, 2 mole), 4-cyanophenol (238.2 g, 2 mole), potassium carbonate (331.7 g, 1,2 eq.) and *N*,*N*-dimethylacetamide (1.0 L) were added under a flow of dry argon to a 2-L three necked flask equipped with a mechanical stirrer. The reaction mixture was stirred for 20 hours at room temperature and poured into 4 L of distilled water. The precipitate was separated under reduced pressure and washed three times with distilled water (3x300 ml). The product was dried at 80 °C for 12 h. The yield was 97% (475.7 g).

^{1}H NMR (600 MHz, DMSO-d_6, δ): ppm 7.35 (d, 2H, J=8.09 Hz), 7.59 (d, 1H, J=8.69 Hz), 7.91 - 8.02 (m, 3H), 8.18 (d, 1H, J=8.67 Hz).

^{13}C NMR (151 MHz, DMSO-d_6, δ): ppm 108.20, 110.29, 115.71, 116.20, 117.43, 118.82, 120.88, 124.40, 124.69, 135.51, 136.91, 158.62, 159.65.

Calculated (%): C 73.46, H 2.88, N 17.13; found (%): C 73.50, H 2,98, N 17.03.

Composite fabrication

Powdered resin PN-30a was applied on a carbon fabric and evenly distributed over the surface with a hot iron. Prepreg sheets 300 × 300 (±3) mm in size (10 layers) were laid on a steel tooling inside a silicone frame 300 × 300 × 5 mm resin upwards. On top the prepreg sheets were covered with a dry layer of fabric, and a steel couling plate of 300 × 300 × 2 mm was placed on top of the preform to create a smooth sample surface. On top a Nialon® IP 340 A drainage material (450 × 550 mm) was laid to facilitate air pumping. Around the tooling a vacuum bag was assembled as follows: at a distance of 150 ± 5 mm from the plied prepreg layers a vacuum film was fixed using a sealing tape; on one side of the bag a silicone tube for pumping air was fixed. Vacuum < 1 Torr was created inside the bag and it was placed in a press and heated to 140 °C at a rate of 2 K min^{-1}. Then pressure of 7.5 bar was applied and the temperature was raised to 180 °C. When the temperature reached 180 °C, the pressure was raised to 20 bar and the sample was kept under these conditions for 8 h. Afterwards, the composite was cooled at a rate of no more than 5 K min^{-1} and the mold was disassembled. The sample was post-cured free-standing at 330 °C or 375 °C for 8 h.

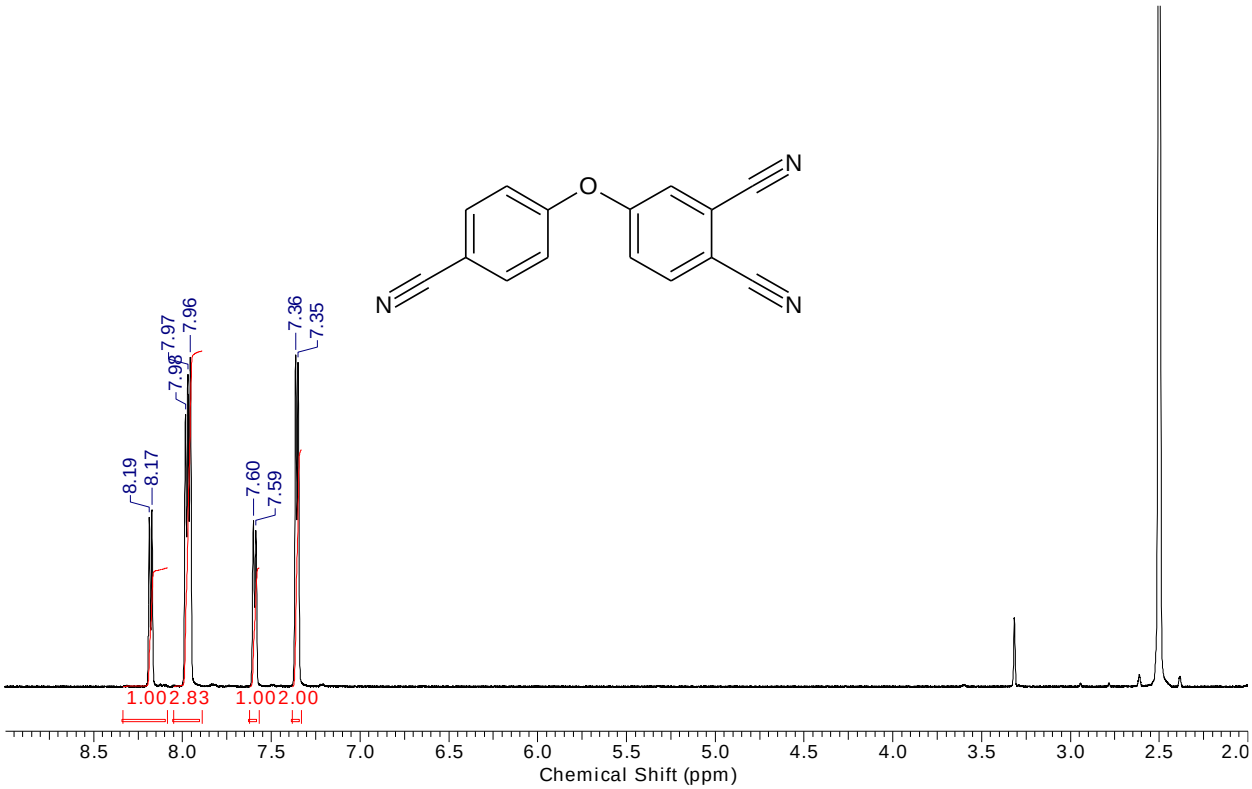

Figure S1. ^{1}H NMR spectrum of **CPN**

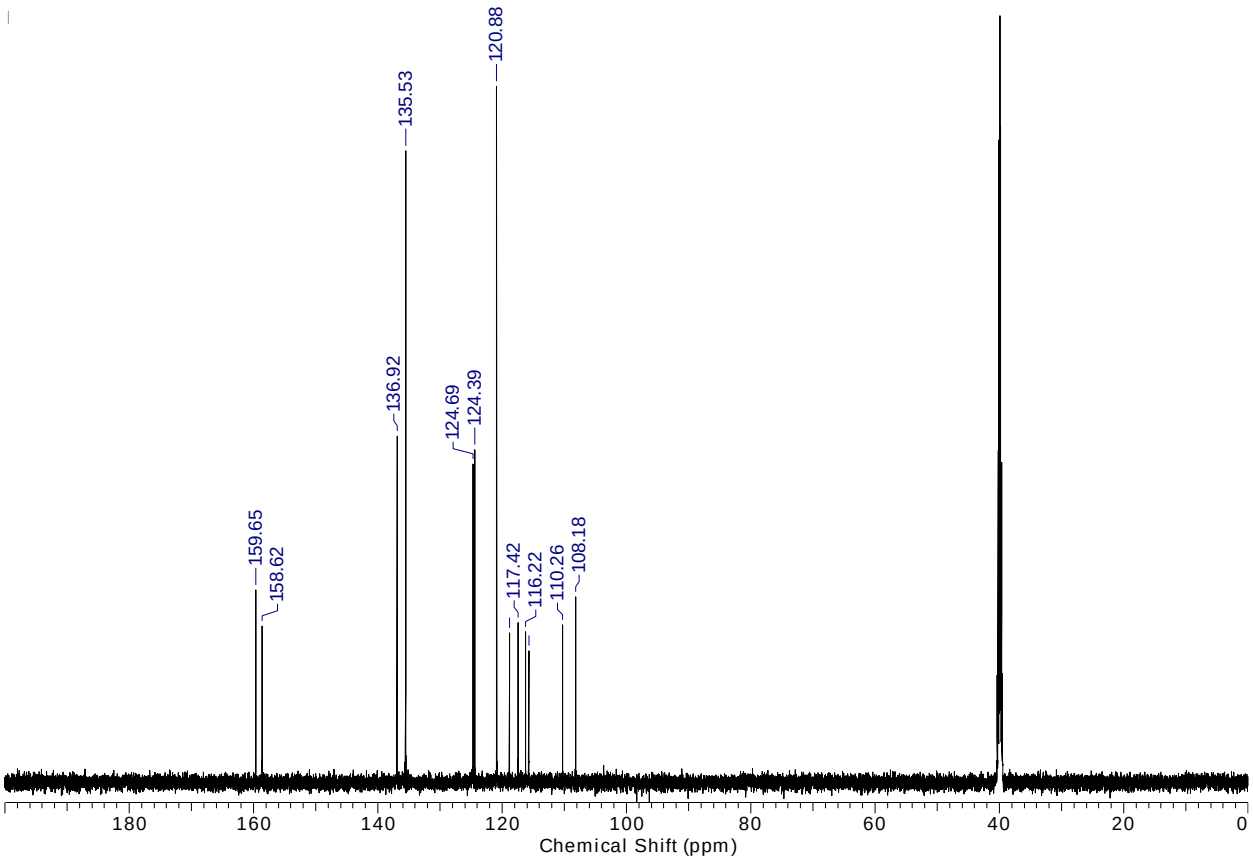

Figure S2. ^{13}C NMR spectrum of **CPN**

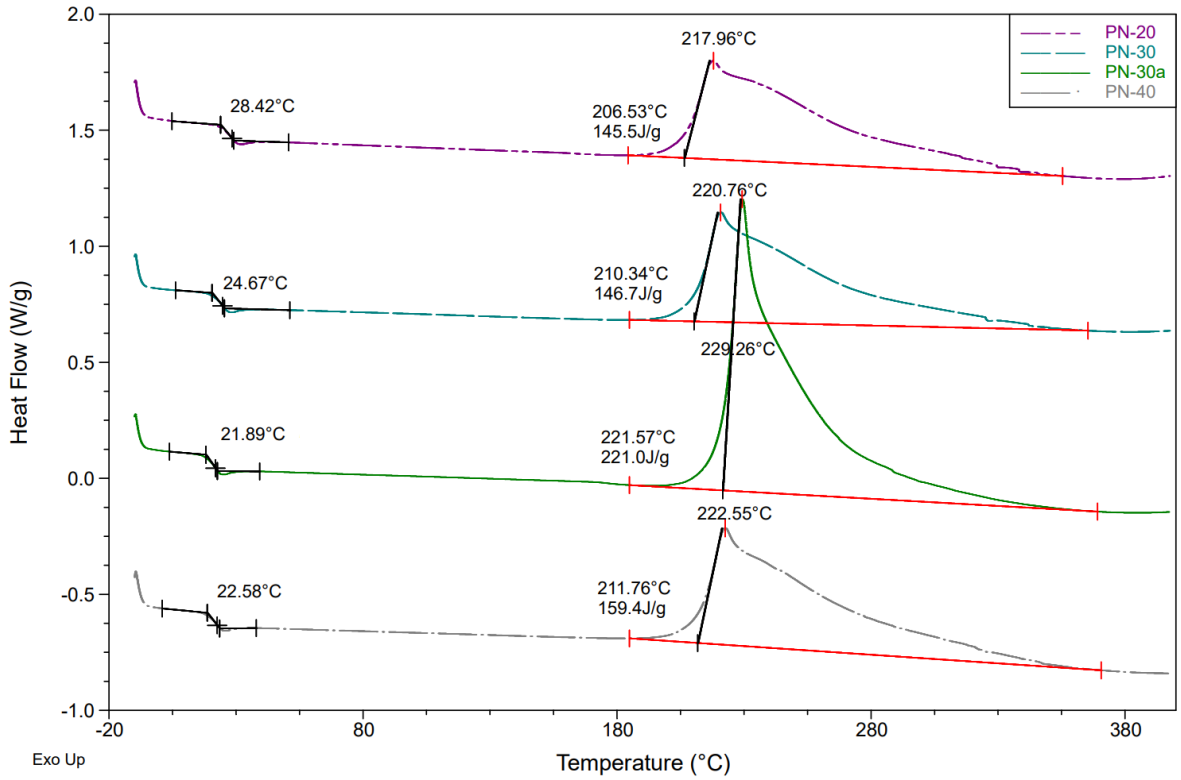

Figure S3. DSC curves of the studied mixtures

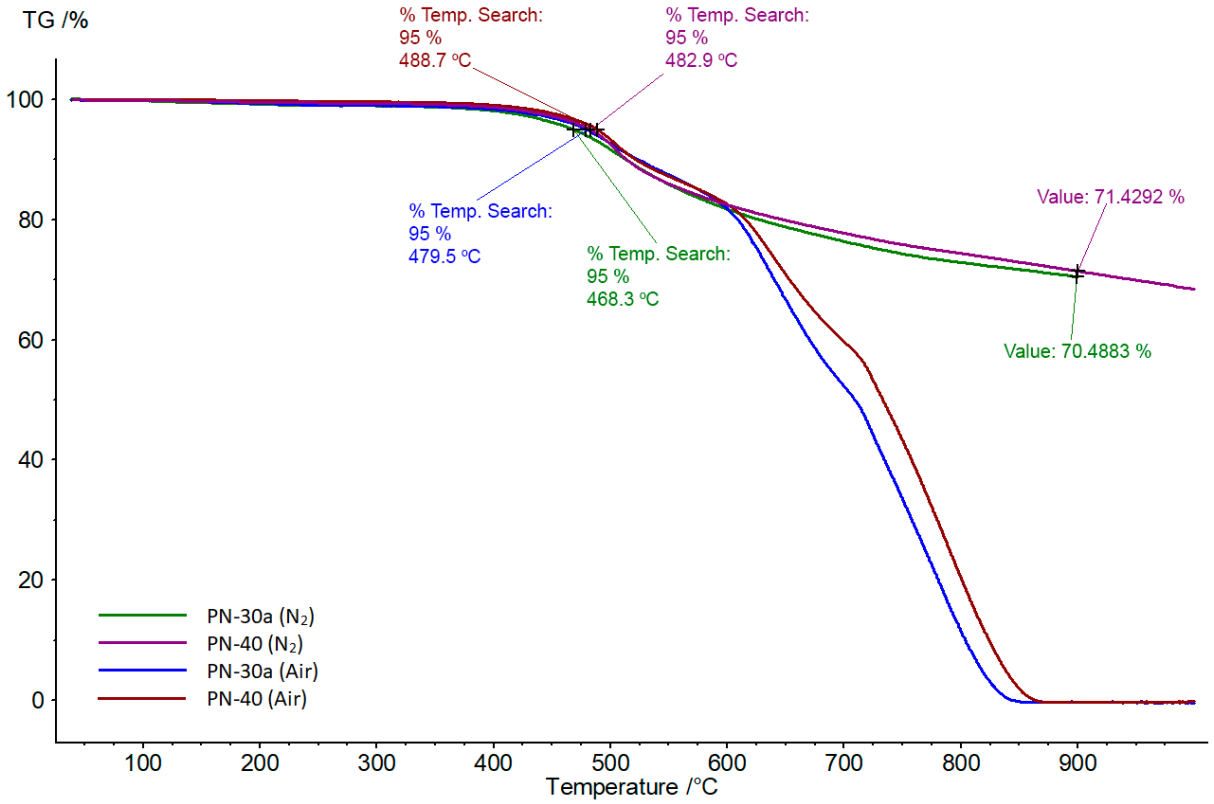

Figure S4. TGA curves for thermosets PN-30a and PN-40 post-cured at 330 °C

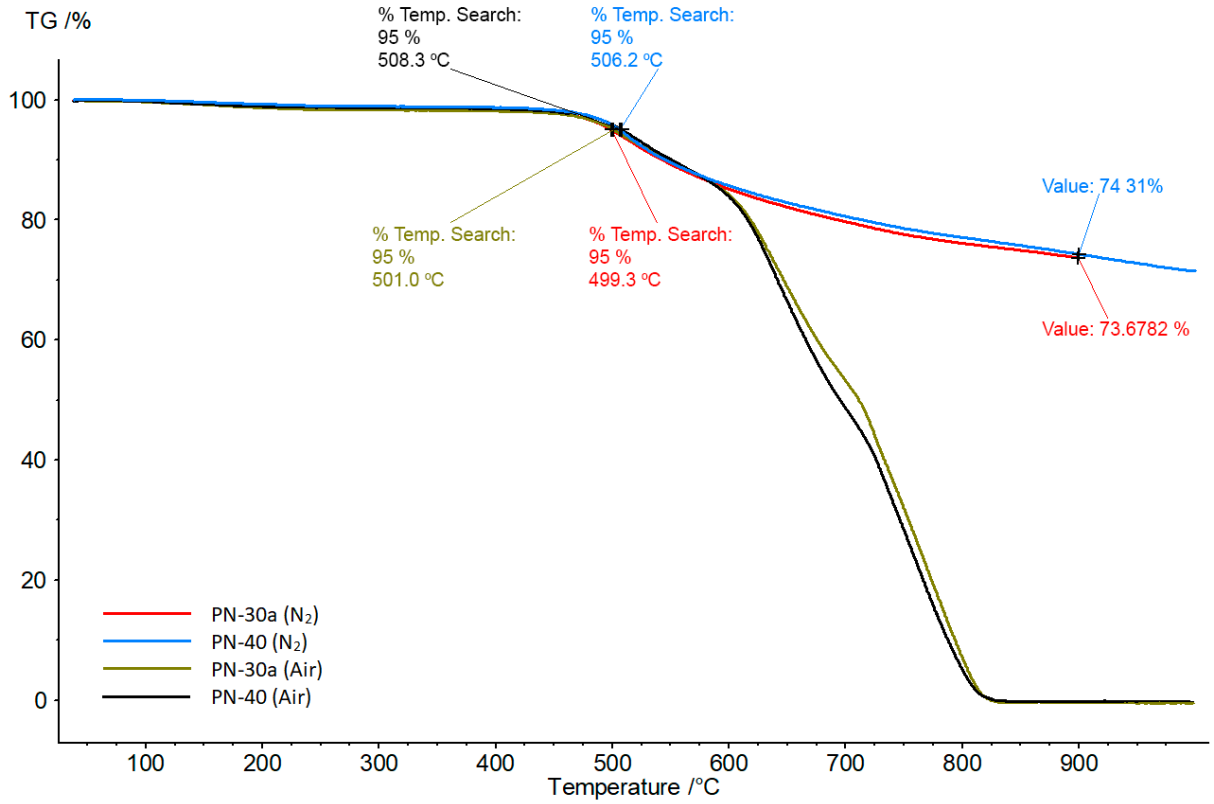

Figure S5. TGA curves for thermosets PN-30a and PN-40 post-cured at 375 °C

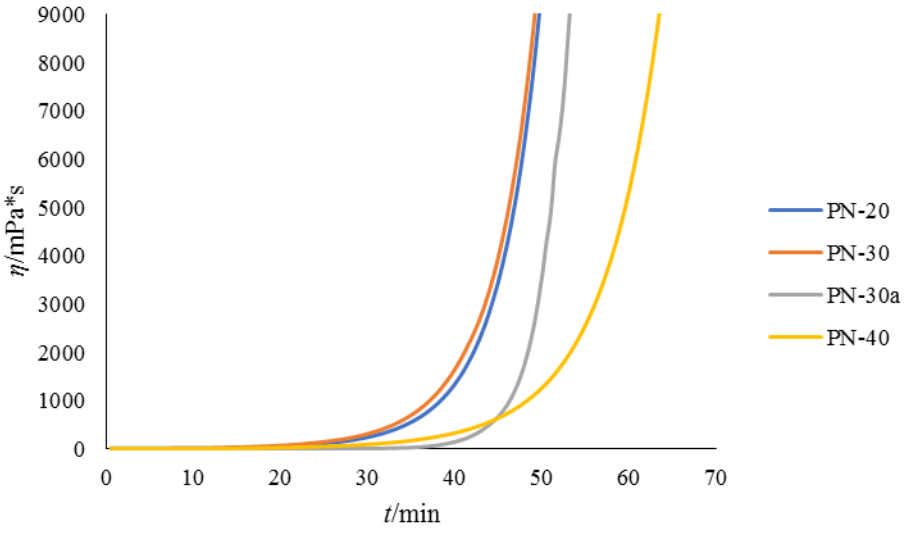

Figure S6. Viscosity isotherms for the studied blends at 180 °C

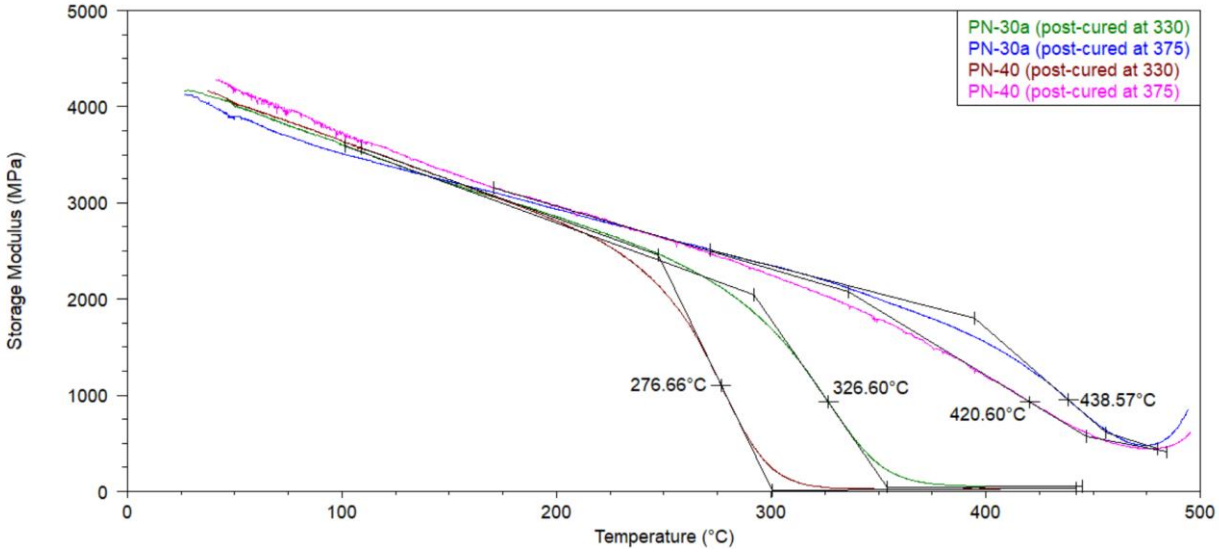

Figure S7. DMA curves of resins cured at 330 and 375 °C