

Supporting Information

**A Synergistic Compatibilization Strategy for NBR/PA6
Blends with Ethylene – Butadiene – Fluorostyrene
Multiblock Terpolymer**

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Content

| | |
|--|-----|
| Typical polymerization procedures. | S3 |
| Preparation of Filled NBR/PA6 Composites. | S4 |
| Preparation of Carbon Black Filled Vulcanizates. | S5 |
| Calculation of the mass fraction crystallinity of PA6 in the blends. | S5 |
| Figure S1. ^{13}C NMR spectrum of PBD (Table 1, entry 4) (CDCl_3 , 25 °C)..... | S6 |
| Figure S2. ^{13}C NMR spectrum of $\text{P}(\text{S}^{\text{F}})$ (Table 1, entry 6) ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C). | S7 |
| Figure S3. DSC curve of $\text{poly}(\text{S}^{\text{F}})$ afforded by complex 2 (Table 1, entry 6)..... | S7 |
| Figure S4. GPC curve of $\text{poly}(\text{E-BD-S}^{\text{F}})$ afforded by complex 2 (Table 2, entry 8).. | S8 |
| Figure S5. GPC curve of $\text{poly}(\text{E-BD-S}^{\text{F}})$ afforded by complex 2 (Table 2, entry 9).. | S8 |
| Table S1. Copolymerization of S^{F} and E using complex 2 | S9 |
| Table S2. Copolymerization of S^{F} and BD using complex 2 | S9 |
| Figure S6. ^{13}C NMR spectrum of $\text{poly}(\text{BD-S}^{\text{F}})$ (Table S2, entry 1) ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C). | S10 |
| Table S3. Terpolymerization of E, BD and St | S10 |
| Figure S7. GPC curve of $\text{poly}(\text{E-BD-S}^{\text{F}})$ afforded by complex 1 (Table 2, entry 1). | S11 |
| Figure S8. GPC curve of $\text{poly}(\text{E-BD-S}^{\text{F}})$ afforded by complex 2 (Table 2, entry 10). | S12 |
| Figure S9. DSC curve of $\text{poly}(\text{E-BD-St})$ afforded by complex 2 (Table S3, entry 2). | S12 |
| Figure S10. DSC curve of $\text{poly}(\text{E-BD-S}^{\text{F}})$ afforded by complex 2 (Table 2, entry 4). | S13 |
| Table S4. Water contact angles of P2 after acidification and alkalization | S13 |
| Figure S11. ^1H NMR spectrum of $\text{poly}(\text{E-BD-S}^{\text{F}})$ (Table 2, entry 4) ($\text{C}_2\text{D}_2\text{Cl}_4$, 110°C). | S14 |
| Figure S12. EDS mapping results and analysis of fluorine (F) content in NBR/PA6 blends with different compatibilizer loadings..... | S14 |
| Figure S13. EDS line scan results and analysis for NBR/PA6/ P3 (100/40/10 wt%) blend..... | S15 |
| Figure S14. DMA curves versus temperature curves for NBR/PA6 blends..... | S15 |
| Figure S15. $\text{C}1\text{s}$ and $\text{S}2\text{p}$ XPS spectra of NBR/PA6/ P3 (100/40/1.5) blend. | S16 |

| | |
|---|-----|
| Table S5. Relative area percentages of C1s peaks corresponding to different functional groups..... | S16 |
| Table S6. Relative area percentages of different sulfur species in the S2p region.... | S16 |
| Figure S16. Mechanical properties of various blends. | S16 |

Typical polymerization procedures.

Typical Procedure for Homopolymerization of butadiene or *para*-fluorostyrene.

Under a nitrogen atmosphere and room temperature, catalyst **1-2** (10 μmol , 3 mL toluene) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (9.2 mg, 10 μmol , 1 mL toluene) were mixed together and react for a few minutes to give an orange solution, then a solution of monomers (butadiene or styrene) and corresponding Al^iBu_3 was added into it and kept stirring for a designed time. The reaction mixture was poured into a large quantity of ethanol and then dried under vacuum at ambient temperature to give a constant weight.

Typical Procedure for Homopolymerization of Ethylene.

Homopolymerization of ethylene was carried out in a 150 mL autoclave with a magnetic stirred bar. In the glove box, a 30 mL toluene solution and corresponding Al^iBu_3 were added into a compressive resistance reactor containing a magnetic stirring bar, the reactor was taken out of glove box and was linked up to ethylene gas pipelines, and set in the thermo-stated oil bath (40 $^\circ\text{C}$). The solution was degassed and then saturated with ethylene (4 atm) for three times under vigorous stirring, then a 2 mL toluene solution of catalyst **1-2** (10 μmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (10 μmol) was transferred into it quickly by syringe through a three-way valve under ethylene blowing, the polymerization was quenched after designed time by ethanol. The precipitated polymer was filtered and washed with ethanol, and then dried under vacuum at 40 $^\circ\text{C}$ until the weight has no change.

Typical Procedure for Tercopolymerization of Ethylene, Butadiene and *para*-fluorostyrene.

Tercopolymerization of ethylene, butadiene and styrene were carried out in a 150 mL autoclave with a magnetic stirred bar. In the glove box, a toluene solution of butadiene, *para*-fluorostyrene and corresponding AlⁱBu₃ were added into a compressive resistance reactor containing a magnetic stirring bar, the reactor was taken out of glove box and was linked up to ethylene gas pipelines, and set in the thermo-stated oil bath (40 °C). The solution was degassed and then saturated with ethylene (4 atm) for three times under vigorous stirring, then a 2 mL toluene solution of catalyst **2** (10 μmol) and [Ph₃C][B(C₆F₅)₄] (10 μmol) was transferred into it quickly by syringe through a three-way valve under ethylene blowing, the polymerization was quenched after designed time by ethanol. The precipitated polymer was filtered and washed with ethanol, and then dried under vacuum at 40 °C until the weight has no change. The ethylene content and the butadiene content was calculated according to the following equation (The integrals are in terms of hydrogens of I_{5.06-5.16} as 2 and *n* represents the mole fraction of this monomer in the total polymer sequence):

$$n_S^F = I_{6.60-7.40} / 4 ;$$

$$n_{BD} = (I_{5.50-6.00} - 1) / 2 + 1; \quad n_E = \{I_{1.21-2.40} - [(I_{5.50-6.00} - 1) / 2] * 4 - 3 * n_S^F - 3\} / 4$$

$$f_S^F = 0.2 / (n_S^F + n_{BD} + n_E) * 100%; \quad f_{BD} = n_{BD} / (n_S^F + n_{BD} + n_E) * 100%;$$

$$f_E = n_E / (n_S^F + n_{BD} + n_E) * 100%;$$

where I_{6.60-7.40} ppm is the total peak area of protons at 6.60-7.40 ppm in the ¹H NMR spectra.

Preparation of Filled NBR/PA6 Composites.

A typical formulation of carbon black filled composites is respectively, the details are summarized in Table 1 below:

■ Stage 1: NBR Masterbatch Mixing

The process commenced in an internal mixer at 60 °C and 80 rpm. NBR was loaded and mixed for 2 minutes. Subsequently, half of the carbon black and half of the minor ingredients were added and mixed for 1 minute, followed by the addition of the remaining halves for another 2 minutes. The compound was dropped after a total mixing time of 8 minutes and then transferred to a two-roll mill for sheet

formation.

■ **Stage 2: PA6 Blending & Compatibilization**

Mixing was conducted in an internal mixer, with the temperature optimized and finally set at 220 °C. The rotors were set at 80 rpm and 60 rpm. PA6 was added and melted over 4 minutes. Then, half of the carbon black masterbatch along with the compatibilizer were incorporated and mixed for 1 minute. The remaining masterbatch was added and mixed for 1 minute at 60 rpm. The batch was dropped 1 minute later and sheeted on a two-roll mill.

- Then the sulfur, accelerator CZ were introduced in portions on a two-roll mill at 60 °C.

Table 1. Formulations of Filled Rubber Composites (phr)

| Entry | NBR/PA6 | NBR/PA6/P3 |
|--|----------------|-------------------|
| NBR | 100 | 100 |
| PA6 | 40 | 40 |
| P3 | - | 1.5/5/10 |
| ZnO | 5 | 5 |
| stearic acid | 1.0 | 1.0 |
| 2,6-Di-tert-butyl-4-methylphenol | 1.5 | 1.5 |
| accelerator CZ | 2.5 | 2.5 |
| N-1,3-dimethylbutyl-N'-phenyl- p-phenylenediamine | 1.5 | 1.5 |
| Rhenogran S-80 | 1 | 1 |
| carbon black | 40 | 40 |

Preparation of Carbon Black Filled Vulcanizates.

The black carbon filled rubber composites were kept at room temperature for 24 h and then were cured at 180 °C for optimum curing time (t_{90}) under 10 MPa pressure.

Calculation of the mass fraction crystallinity of PA6 in the blends.

The mass fraction crystallinity of PA6 in the blends after isothermal crystallization was calculated using the temperature dependent Dh values for fully amorphous and fully crystalline PA6 available from the ATHAS databank according to:

$$\omega_c(T) = \frac{\Delta h_{\text{exp}}(T)}{\Delta h(T)}$$

In case of calculating the crystallinity from the melting peak, T was taken equal to T_m (peak max) and recrystallization exotherms were subtracted for calculating Dh_{mexp}. For this calculation, the denominator of Eq. (1), Δh(T), for the monoclinic g-phase of PA6 was taken equal to that of the monoclinic a-phase of PA6. This is justified by literature data: Δh(T_m)_{a-phase} = 230 J/g and h(T_m)_{a-phase} = 239 J/g.

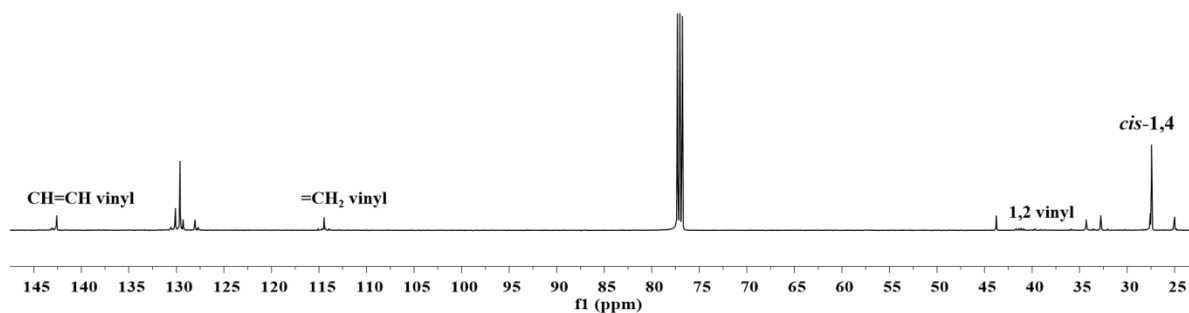


Figure S1. ¹³C NMR spectrum of PBD (Table 1, entry 4) (CDCl₃, 25 °C).

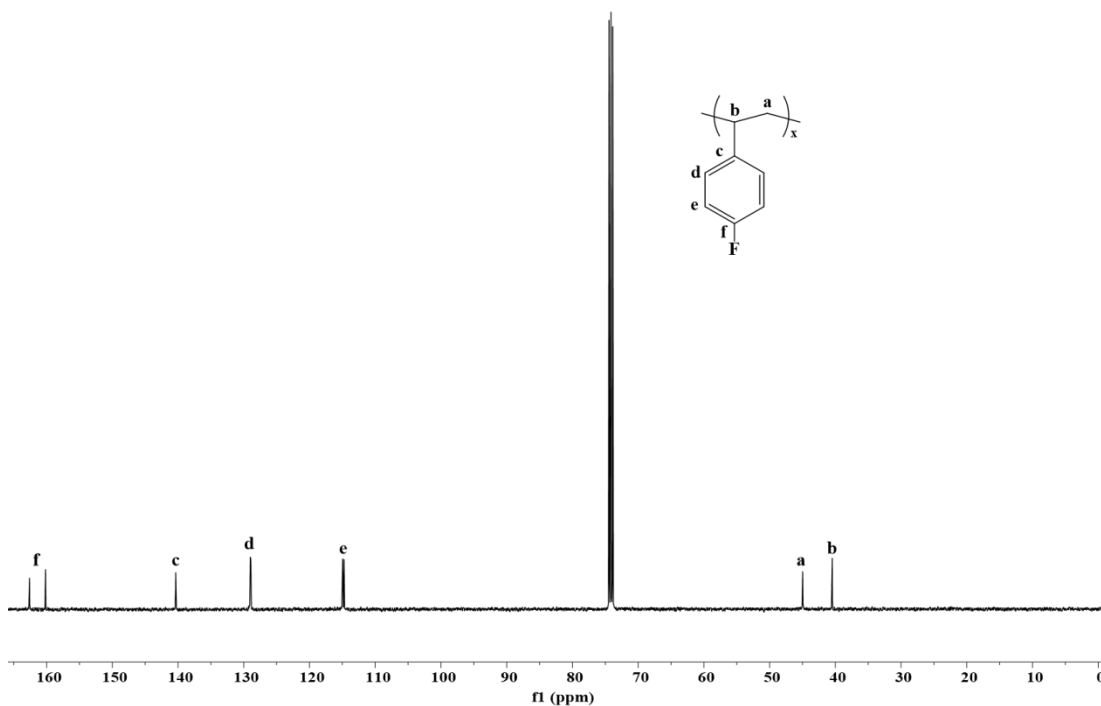


Figure S2. ^{13}C NMR spectrum of $\text{P}(\text{S}^{\text{F}})$ (Table 1, entry 6) ($\text{C}_2\text{D}_2\text{Cl}_4$, $110\text{ }^\circ\text{C}$).

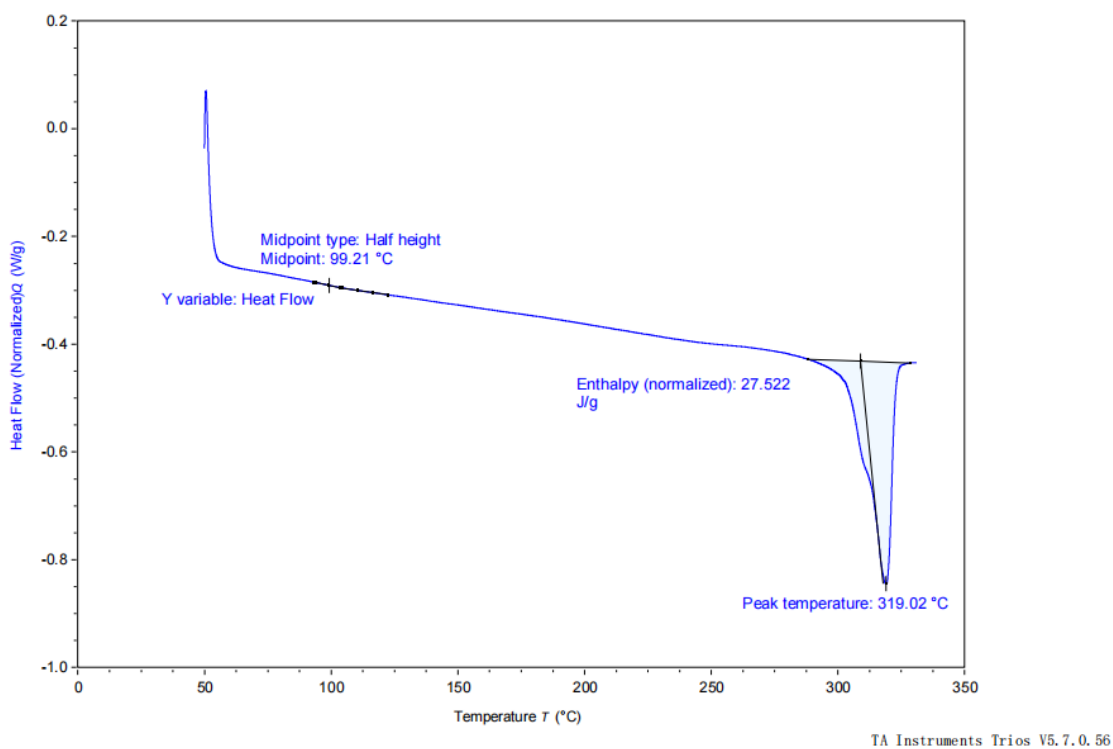


Figure S3. DSC curve of $\text{poly}(\text{S}^{\text{F}})$ afforded by complex **2** (Table 1, entry 6).

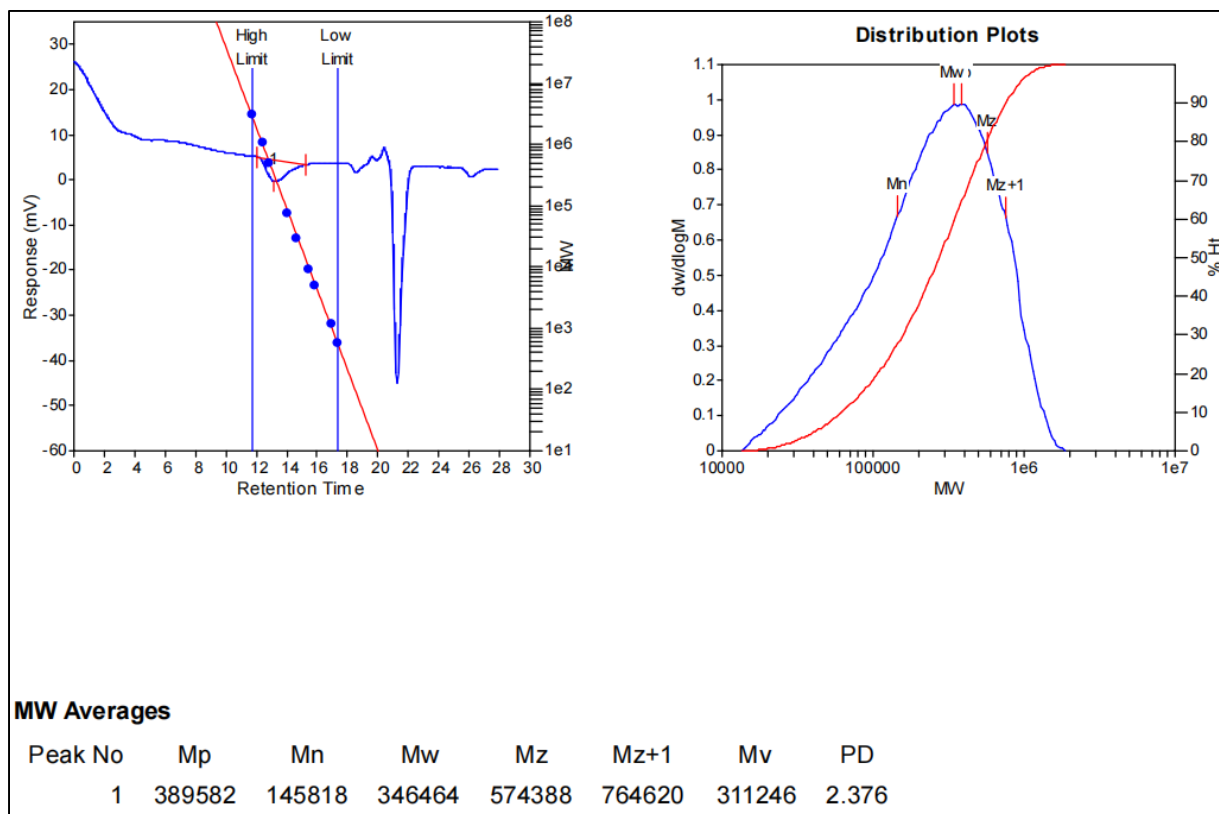


Figure S4. GPC curve of poly(E-BD-S^F) afforded by complex **2** (Table 2, entry 8).

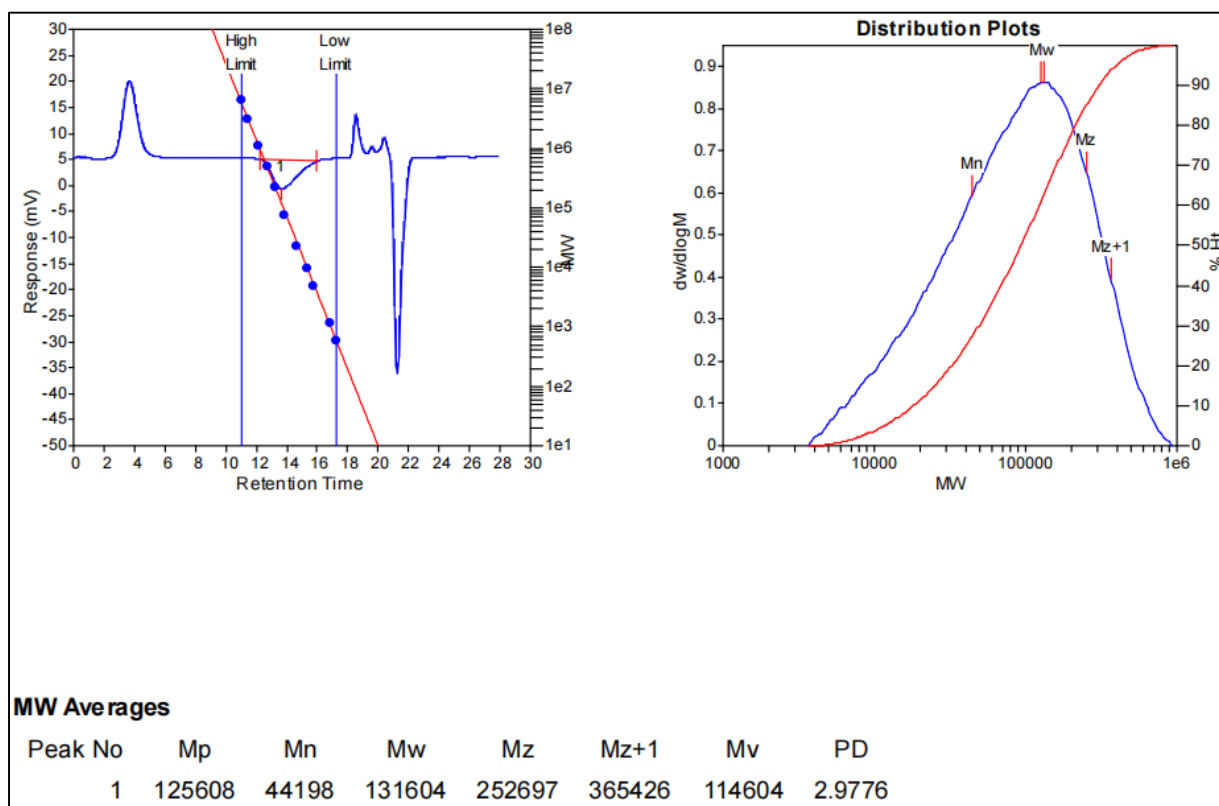


Figure S5. GPC curve of poly(E-BD-S^F) afforded by complex **2** (Table 2, entry 9).

Table S1. Copolymerization of S^F and E using complex 2

| entry ^a | Cat. | [SF] ₀ [mol/L] | Yield[g] |
|--------------------|------|---------------------------|----------|
| 1 | 2 | 1 | trace |

^aConditions: [Cat.]/[Ph₃C][B(C₆F₅)₄]/[AlⁱBu₃] = 1:1:10 (mol/mol/mol), toluene = 20 mL, complex (10 μmol), temperature 40 °C, E = 4 bar, t=1h.

Table S2. Copolymerization of S^F and BD using complex 2

| entry ^a | Cat | [BD] ₀ [mol/L] | [SF] ₀ [mol/L] | Yield [g] | f_S^{Fb} [mol%] | f_{BD}^b (<i>cis</i> -1,4/1,2) [mol%] | M_n^c [10 ⁴] | M_w/M_n^c | T_g/T_m^d [°C] |
|--------------------|-----|------------------------------|------------------------------|--------------|----------------------|--|-------------------------------|-------------|---------------------|
|--------------------|-----|------------------------------|------------------------------|--------------|----------------------|--|-------------------------------|-------------|---------------------|

^aConditions: [Cat.]/[Ph₃C][B(C₆F₅)₄]/[AlⁱBu₃] = 1:1:10 (mol/mol/mol), toluene = 20

| | | | | | | | | | |
|---|---|-----|-----|------|-----|---------------------|------|-----|---------|
| 1 | 2 | 2.0 | 1.0 | 1.88 | 6.7 | 93.3 (74.7/25.3) | 26.5 | 1.7 | -10.9/- |
|---|---|-----|-----|------|-----|---------------------|------|-----|---------|

mL, complex (10 μ mol), temperature 40 $^{\circ}$ C, E = 4 bar, t = 1h. ^bMeasured by ¹H and ¹³C NMR in C₂D₂Cl₄ at 110 $^{\circ}$ C. ^cMeasured by GPC in 1,2,4-trichlorobenzene at 150 $^{\circ}$ C using the polystyrene standard. ^dDetermined by DSC.

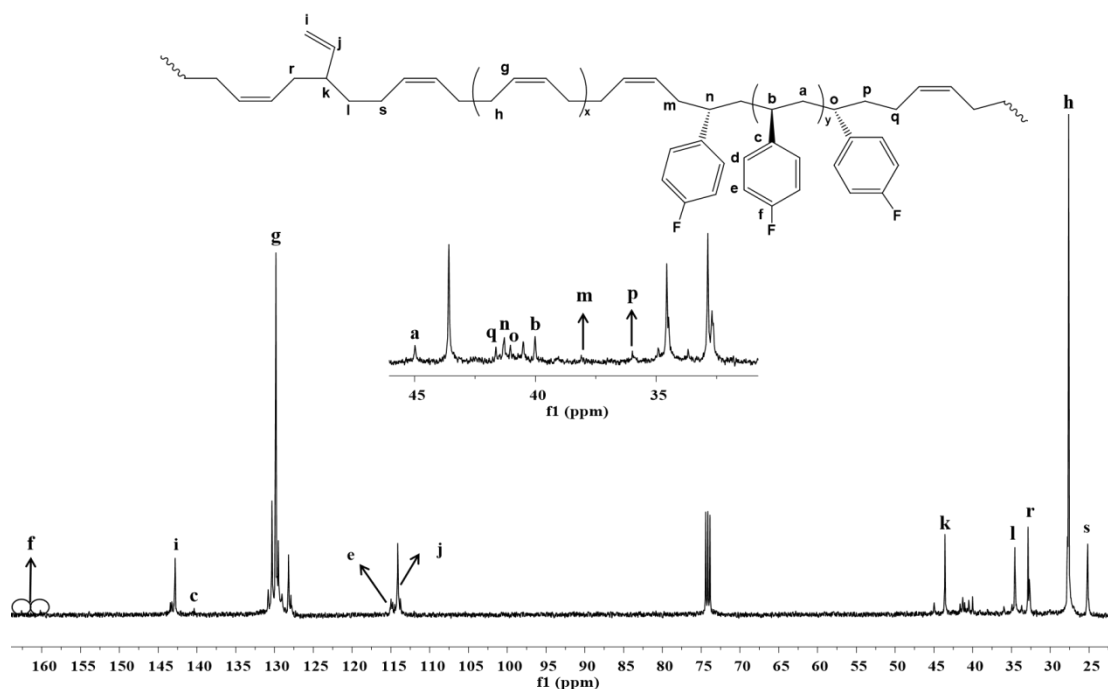


Figure S6. ¹³C NMR spectrum of poly(BD-S^F) (Table S2, entry 1) (C₂D₂Cl₄, 110 $^{\circ}$ C).

Table S3. Terpolymerization of E, BD and St

| Run ^a | Cat. | [BD] ₀ [mol/L] | [St] ₀ [mol/L] | Yield [g] | f_{BD}^b (<i>cis</i> -1,4/1,2) [mol%] | f_{St}^b [mol%] | f_E^b [mol%] | M_n^c [10 ⁴] | PDI ^c | T_g/T_m^d [$^{\circ}$ C] |
|------------------|------|------------------------------|------------------------------|--------------|--|----------------------|-------------------|-------------------------------|------------------|--------------------------------|
| 1 | 1 | 2.00 | 1.00 | 1.62 | 85.7(84.1/15.9) | 1.4 | 12.9 | 28.8 | 1.8 | -90.2/128.9 |

2 2 2.00 1.00 1.45 85.5(75.1/24.9) 1.3 13.2 17.2 1.9 -85.2/-

^aConditions: [Cat.]/[Ph₃C][B(C₆F₅)₄]/AlⁱBu₃ = 1:1:10 (mol/mol/mol), toluene = 20 mL, complex (10 μmol), temperature 40 °C, t = 1h. ^bMeasured by ¹H and ¹³C NMR in C₂D₂Cl₄ at 110 °C. ^cMeasured by GPC in 1,2,4-trichlorobenzene at 150 °C using the polystyrene standard. ^dDetermined by DSC.

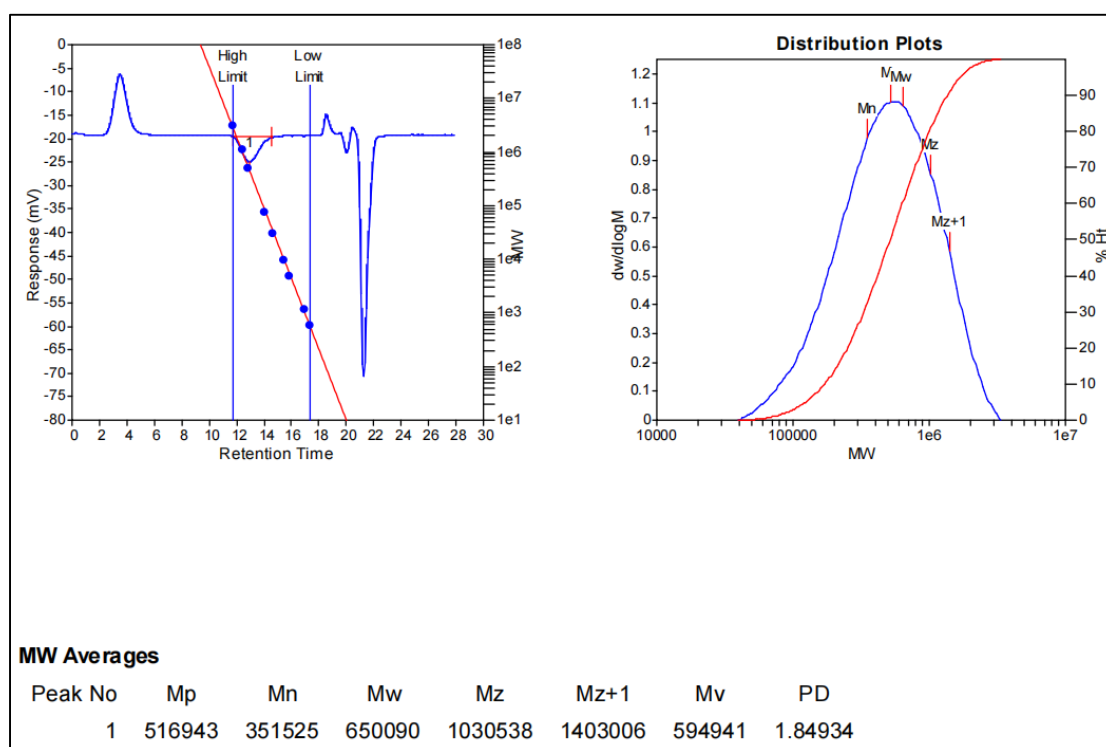


Figure S7. GPC curve of poly(E-BD-S^F) afforded by complex **1** (Table 2, entry 1).

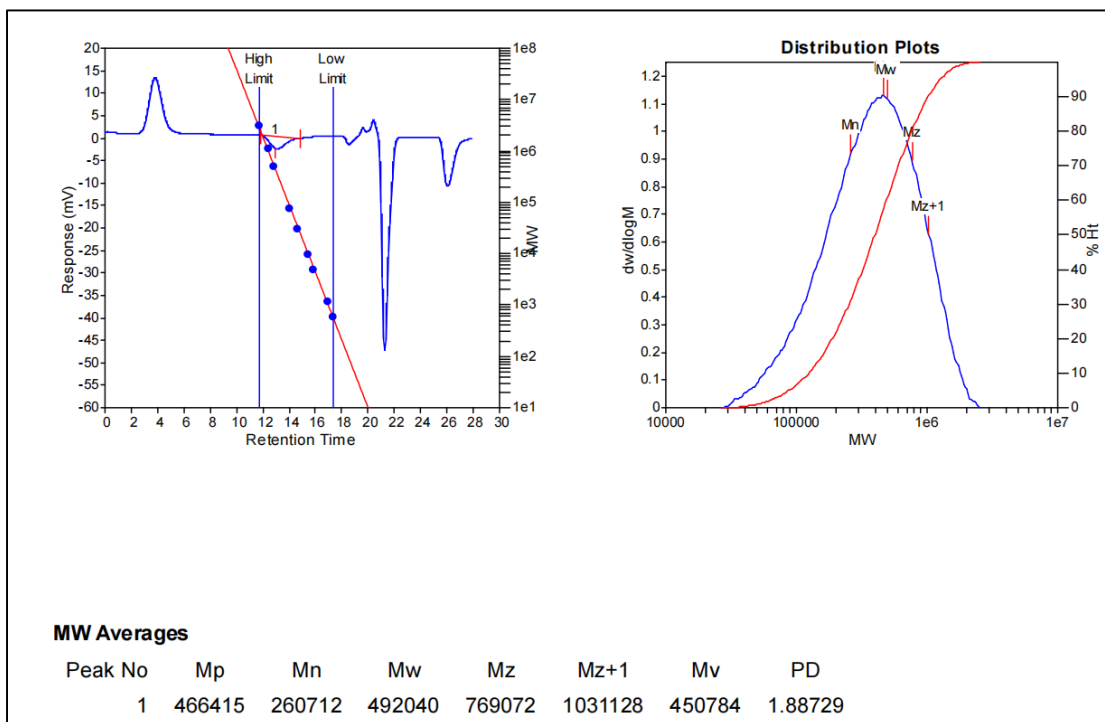


Figure S8. GPC curve of poly(E-BD-S^F) afforded by complex **2** (Table 2, entry 10).

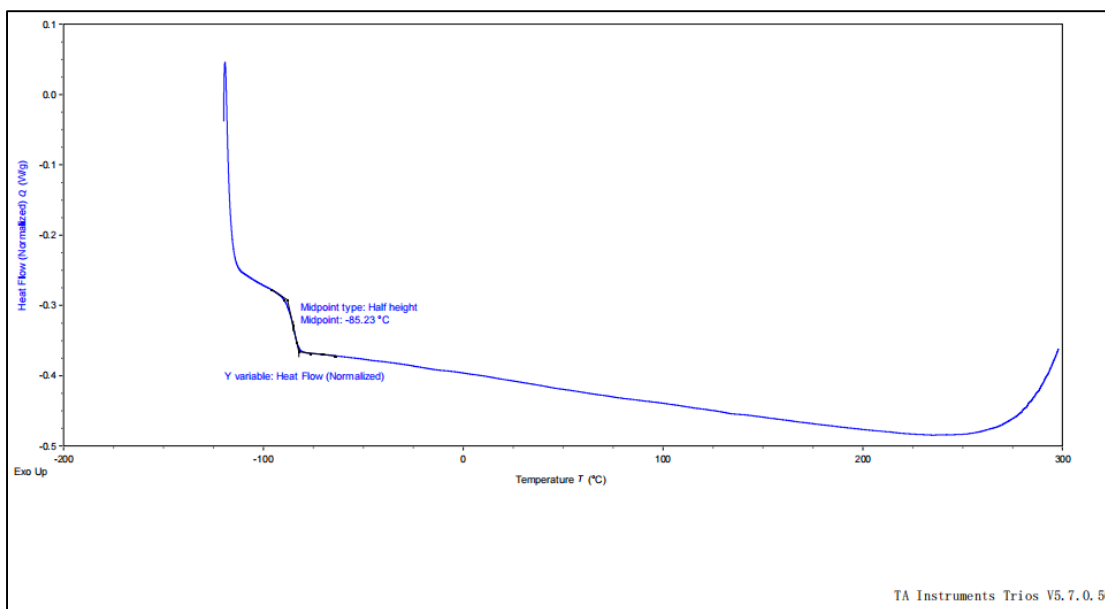


Figure S9. DSC curve of poly(E-BD-St) afforded by complex **2** (Table S3, entry 2).

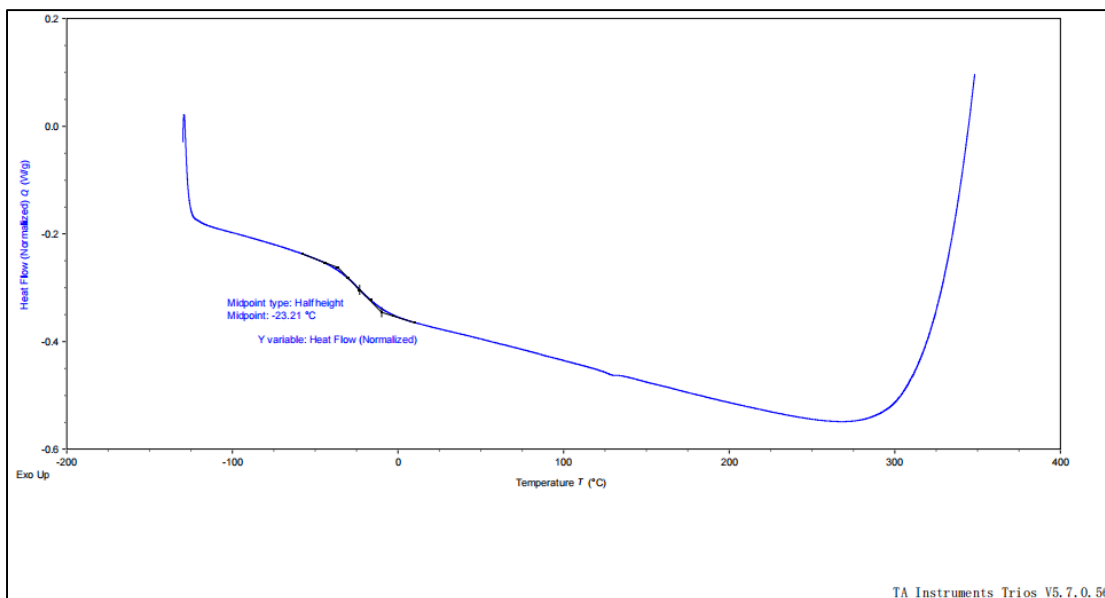


Figure S10. DSC curve of poly(E-BD-S^F) afforded by complex **2** (Table 2, entry 4).

Table S4. Water contact angles of P2 after acidification and alkalization

| Sample | Contact angle (°) | | | | | | | |
|--------|------------------------|------------|------------|------------|------------------------|------------|------------|------------|
| | Acidification (PH = 1) | | | | Alkalization (PH = 13) | | | |
| | 0h | 6h | 9h | 12h | 0h | 6h | 9h | 12h |
| P2 | 121.5±1.94 | 117.2±0.37 | 117.1±1.11 | 117.1±1.33 | 121.5±1.94 | 119.1±0.67 | 118.0±0.36 | 117.9±0.33 |

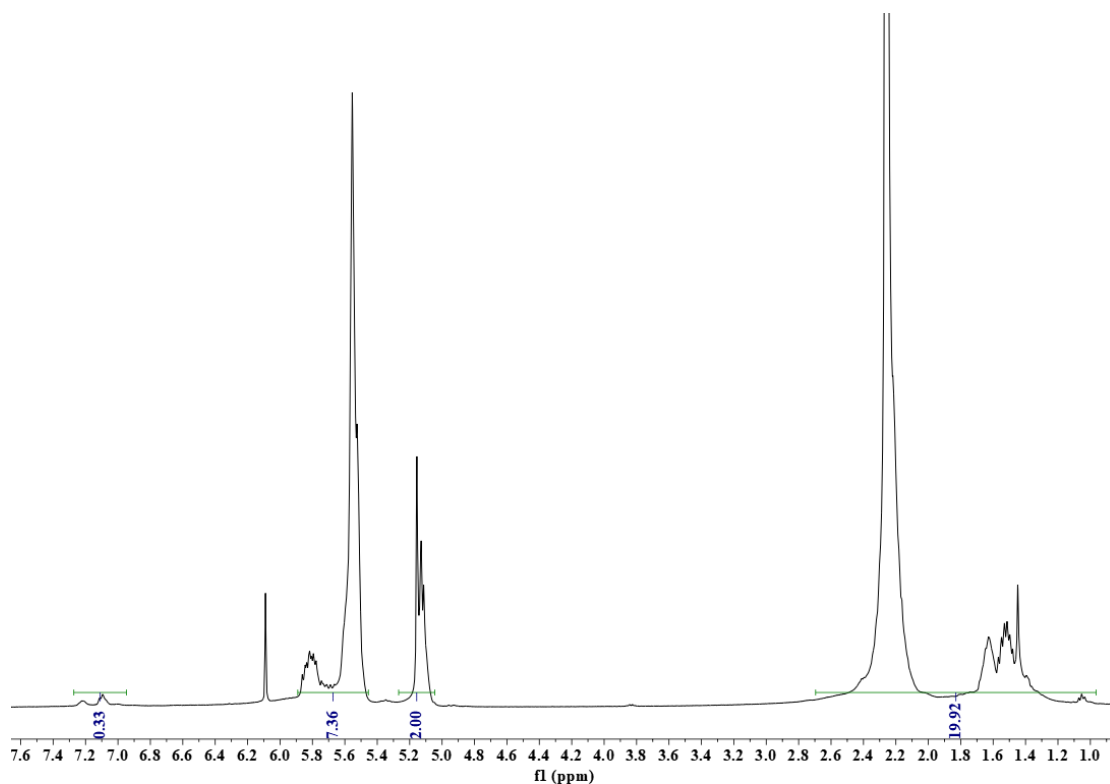


Figure S11. ^1H NMR spectrum of poly(E-BD-S^F) (Table 2, entry 4) ($\text{C}_2\text{D}_2\text{Cl}_4$, 110°C).

| Sample (P3 content) | Figure | Element | Series | Wt% | Wt% Sigma | At% |
|---------------------|--------|---------|--------|-------------|-------------|-------------|
| 1.5 wt% | a | F | K | 0.00 | 0.06 | 0.00 |
| 5 wt% | b | F | K | 0.00 | 0.07 | 0.00 |
| 10 wt% | c | F | K | 0.11 | 0.06 | 0.07 |

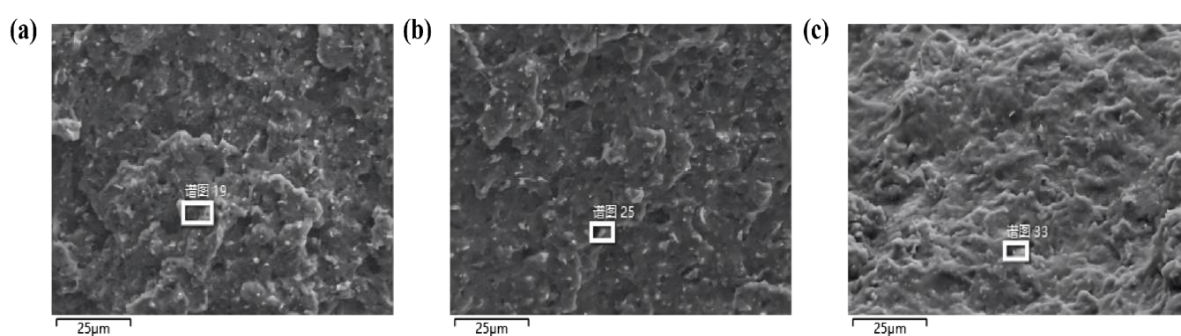


Figure S12. EDS mapping results and analysis of fluorine (F) content in NBR/PA6 blends with different compatibilizer loadings.

| Element | Series | Wt% | Wt% Sigma | At% |
|----------|----------|-------------|-------------|-------------|
| C | K | 60.53 | 0.18 | 67.94 |
| N | K | 5.54 | 0.19 | 5.33 |
| O | K | 30.57 | 0.13 | 25.75 |
| F | K | 0.16 | 0.05 | 0.12 |
| S | K | 0.96 | 0.08 | 0.40 |
| Zn | L | 2.23 | 0.08 | 0.46 |
| Pt | M | 0.00 | | 0.00 |

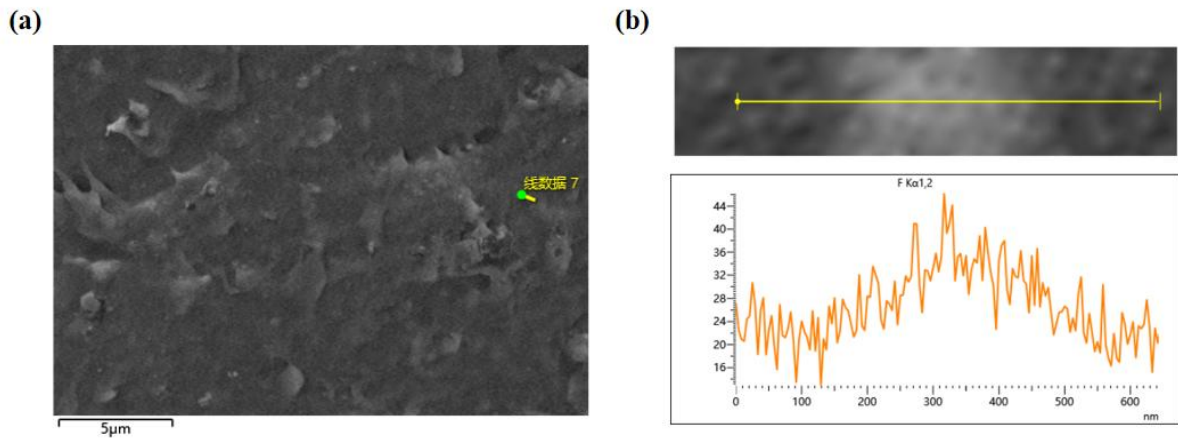


Figure S13. EDS line scan results and analysis for NBR/PA6/P3 (100/40/10 wt%) blend.

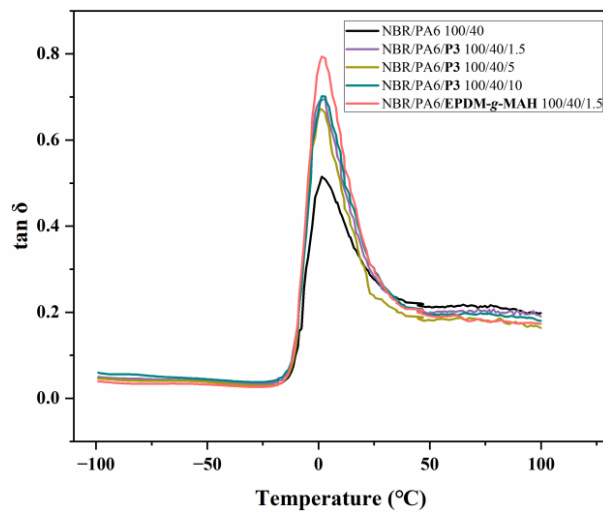


Figure S14. DMA curves versus temperature curves for NBR/PA6 blends.

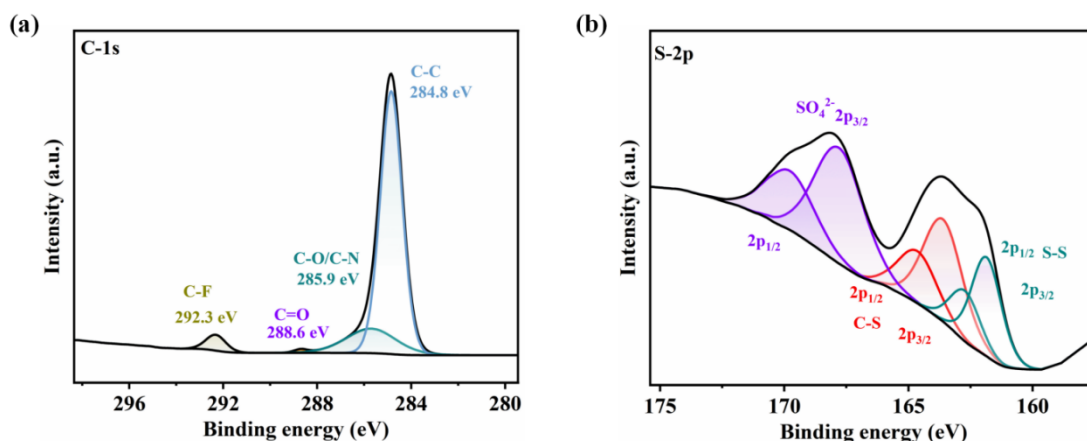


Figure S15. C1s and S2p XPS spectra of NBR/PA6/P3 (100/40/1.5) blend.

Table S5. Relative area percentages of C1s peaks corresponding to different functional groups.

| Sample | Area of C1s peaks (%) | | | |
|-----------------------|-----------------------|-------|-------|------|
| | C-C | C-O | C = O | C-F |
| NBR/PA6/P3 100/40/1.5 | 78.43 | 16.68 | 0.59 | 4.30 |

Table S6. Relative area percentages of different sulfur species in the S2p region.

| Sample | Area of S2p peaks (%) | | |
|-----------------------|-----------------------|-------|-------------------------------|
| | S-S | S-C | SO ₄ ²⁻ |
| NBR/PA6/P3 100/40/1.5 | 23.36 | 31.55 | 45.08 |

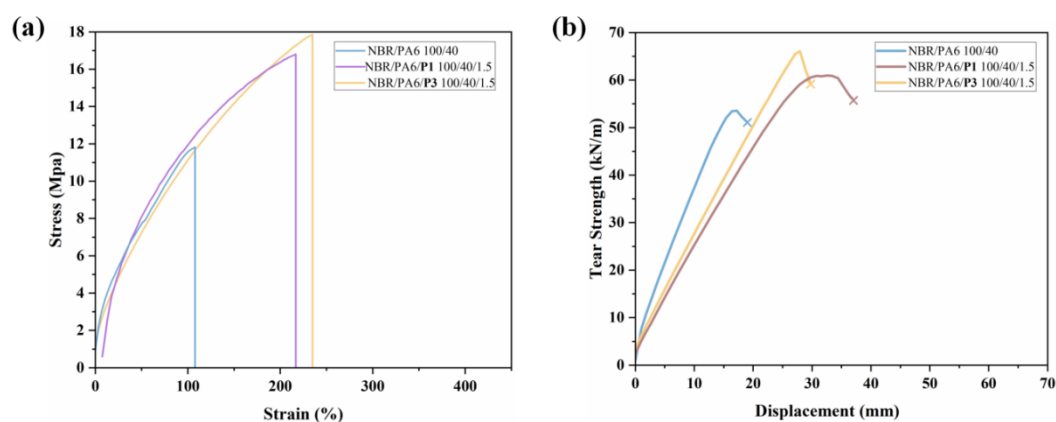


Figure S16. Mechanical properties of various blends. (a) Stress-strain curves. (b) Tear strength curve.