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Research Article

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Posted Date: June 25th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10031195/v1>

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Version of Record: A version of this preprint was published at Journal of Polymer Research on October 20th, 2026. See the published version at <https://doi.org/10.1007/s10965-026-05151-7>.

Toughening Performance of ASA Core-shell Graft Copolymers Constructed with Various Crosslinking Agents on SAN Resins

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Abstract: In this study, poly(butyl acrylate) (PBA) seed latex was prepared through seed emulsion polymerization using five crosslinking agents: dicyclopentanyl acrylate (DCPA), N, N'-methylenebisacrylamide (MBA), ethylene glycol dimethacrylate (EGDMA), diallyl maleate (DMA), and pentaerythritol tetraacrylate (PETA). After grafting, a series of acrylate-styrene-acrylonitrile (ASA) graft polymers were synthesized. The study systematically investigated the effects of different crosslinking agents on the uniformity of ASA structures and their impact on the toughening performance of poly(styrene-co-acrylonitrile) (SAN) resins. The results show that among the various types of crosslinking agents, DMA exhibited the best particle size uniformity and crosslinked structure stability. The grafting rate of ASA graft powder was the highest (34.6%). In the SAN/ASA (35/25) blend system, ASA particles crosslinked with DMA increased the impact strength to 21.7 kJ/m², more than six times higher than that of pure SAN, with an elongation at break of 28.44%. The impact fracture surface was rough with evenly distributed pores, demonstrating excellent toughness. In summary, different types of crosslinking agents have varying effects on

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particle size, crosslinking density, and the toughening effect of ASA on SAN resins.

This study provides a theoretical basis and experimental reference for the formulation design of high-performance ASA resins and the toughening of SAN resins.

Keywords: seed emulsion polymerization, graft copolymers, crosslinking agents, grafting degree, SAN/ASA blends, mechanical properties

1. Introduction

In the field of high-end engineering plastics, automotive exterior parts need to withstand erosion from ultraviolet rays, acid rain, and sand, while outdoor building materials need to maintain their appearance and mechanical performance over the long term. These application scenarios impose stringent requirements on the weather resistance and mechanical properties of the materials. Poly(styrene-co-acrylonitrile) (SAN), as an important thermoplastic resin material [1-4], has high rigidity, chemical resistance, solvent resistance, good chemical stability, and excellent thermal processability, but its inherent brittleness and low notch impact strength seriously limit its application in the aforementioned high-end scenarios [5-9]. Traditionally, to improve the impact resistance of SAN resin materials, they are usually blended with acrylonitrile-butadiene-styrene plastic (ABS). Acrylic ester-styrene-acrylonitrile (ASA) resin, as an upgraded variety of ABS resin, has toughness and rigidity basically comparable to ABS resin, but is significantly superior to ABS resin in weather resistance and durability, becoming the new generation of impact-modified resin.

Currently, existing research has identified numerous factors influencing the weatherability and mechanical properties of ASA resin[10-20],. Zhang et al[21] studied

the different morphologies (multi-lobed, full-shell, dumbbell-shaped) resulting from varying amounts of crosslinking agents and found that the toughening efficiency was highest when a complete core-shell structure was formed and the shell composition was close to the SAN matrix. When 30 wt% of ASA particles with a particle size of about 400 nm were added, the notch impact strength of the SAN resin increased significantly while the loss in tensile strength was relatively small. Tian et al[22] found that, in the core-shell structured rubber toughener PBA-SAN (poly(n-butyl acrylate)-g-poly(styrene-acrylonitrile)), the content of acrylate rubber (PBA) plays a decisive role in the mechanical properties of the blend. A high PBA content can significantly improve impact toughness and elongation at break, but it will reduce rigidity and heat distortion temperature. Among them, PBA-SAN particles containing 60 wt% PBA (60% rubber core content) can achieve the optimal balance between toughness and rigidity, and are therefore considered the most suitable impact modifier for toughening SAN resin. Furthermore, influencing factors such as rubber content and rubber particle size in polymers have been discussed in other studies[23]. In addition, factors such as the rubber content in the polymer and the size of the rubber particles have been discussed in other studies. However, a systematic and in-depth study on the effects of different crosslinking agents on PBA particle size, conversion rate, controllable reaction temperature conditions, and the mechanical properties of ASA-toughened SAN resins has not yet been conducted[24].

This experiment mainly uses the seed emulsion polymerization method to study[25-28], the preparation of a series of ASA graft copolymer particles using

different crosslinking agents. These particles were then blended with SAN resin in different proportions to thoroughly investigate the changes in the crosslinking structure of PBA caused by different crosslinking agents, and to comprehensively analyze the effect of the synthesized ASA graft copolymer particles on toughening SAN resin [29-32]The research on the preparation of high-performance ASA resin in this paper can further optimize its performance, reduce production costs, and expand its application in other high-end fields.

2 Experimental Section

2.1 Main experimental materials

Butyl acrylate (BA), industrial grade, Styrene (St, Aladdin Reagent Co., Ltd.), Acrylonitrile (AN, industrial grade, PetroChina Jilin Chemical Group Corporation), Ethylenediaminetetraacetic acid tetrasodium salt (EDTA, analytical grade, Shanghai Macklin Biochemical Technology Co., Ltd.), Sodium formaldehyde sulfoxylate (SFS, analytical grade, Shanghai Macklin Biochemical Technology Co., Ltd.), Ferrous sulfate (FeS, analytical grade, Tianjin Fuchen Chemical Reagent Factory), Potassium persulfate (KPS, analytical grade, Tianjin Fuchen Chemical Reagent Factory), Sodium dodecylbenzenesulfonate (SDS, analytical grade, Tianjin Fuchen Chemical Reagent Factory), Cumene hydroperoxide (CHP, analytical grade, Aladdin Reagent Co., Ltd.), tert-Dodecyl mercaptan (TDDM, analytical grade, Tianjin Fuchen Chemical Reagent Factory), Potassium hydroxide (KOH, Aladdin Reagent Co., Ltd.), Anhydrous magnesium sulfate (MgSO_4 , Aladdin Reagent Co., Ltd.), Dicyclopentenyl acrylate (DCPA, analytical grade, Aladdin Reagent Co., Ltd.), N,N'-Methylenebisacrylamide

(MBA, analytical grade, Aladdin Reagent Co., Ltd.), Ethylene glycol dimethacrylate (EGDMA, analytical grade, Aladdin Reagent Co., Ltd.), Diallyl maleate (DMA, analytical grade, Aladdin Reagent Co., Ltd.), Pentaerythritol tetraacrylate (PETA, analytical grade, Aladdin Reagent Co., Ltd.), Deionized water (DDI); Thermoplastic styrene-acrylonitrile copolymer (SAN, Zhenjiang Chimei Chemical Co., Ltd.) .

2.2 Experimental equipment and instruments

Torque rheometer (RS75H, Haake, Germany); Plate vulcanizer (HB400×400×1D, Qingdao Huabo Mechanical Technology Co., Ltd.); Constant-temperature water bath (XMTE-7000, Shanghai Yuhua Technology Co., Ltd.); Digital constant-temperature stirrer (S212, Shanghai Shenshun Biotechnology Co., Ltd.); Vacuum oven (DZF-6050, Shanghai Yiheng Scientific Instrument Co., Ltd.); High-speed centrifuge (LC-LX-H165A, Shanghai Lichen Technology Co., Ltd.); Lange peristaltic pump (BT100-2J, Baoding Lange Co., Ltd.); Particle size analyzer (90Plus, Brookhaven, USA); Fourier-transform infrared spectrometer (INVENIO-R, Bruker, Germany); Electronic tensile testing machine (STS-100KNxing, Xiamen Yishite Company); Izod impact tester (XJUD-5.5, Chengde Jinjian Testing Instrument Co., Ltd.); Differential scanning calorimeter (DSC, FBS-DSC300A, Xiamen FBS Testing Equipment Co., Ltd.); Scanning electron microscope (SEM, JSM-6510, JEOL, Japan).

2.3 Sample preparation

2.3.1 PBA seed latex preparation

First, this experiment uses a 3L pilot-scale reactor with a batch method to prepare PBA seed latex. In the first step, accurately weigh 600 g of butyl acrylate (BA)

monomer, 9 g of SDS, 12 g of crosslinking agent, and 1600 g of deionized water. In the second step, add the prepared chemicals to the experimental setup, which is a 3L three-necked glass reaction vessel equipped with a reflux device, nitrogen purification inlet and outlet, thermometer, and mechanical stirrer. Place the reaction vessel in a constant temperature water bath. In the third step, when the temperature of the constant-temperature water bath is stabilized at 55 °C, add the initiator solution (1.14 g KPS, 75 g deionized water). When the materials begin the polymerization reaction and the temperature rises to the peak, cool down to 80 °C, maintain the jacket temperature at 80 °C, and continue the reaction for three hours. Preparation of PBA latex with different types of crosslinkers, as shown in Figure 1

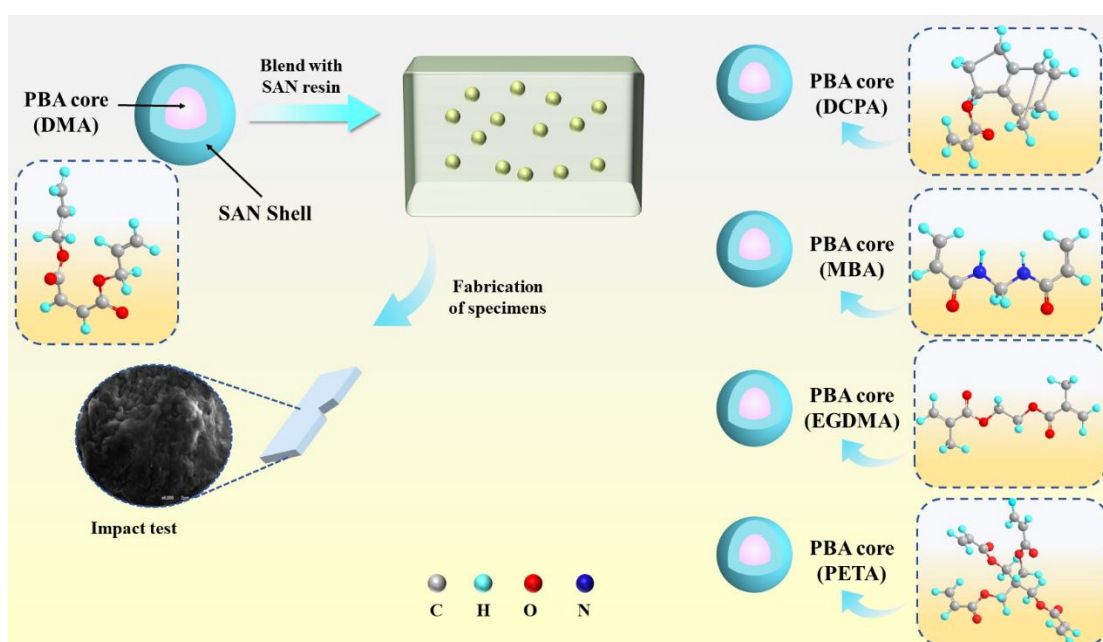


Figure 1 Prepare PBA latex using different types of crosslinking agents, and synthesize ASA particles to modify SAN resin

2.3.2 Preparation of ASA graft powder particles

This experiment mainly used a semi-continuous method to prepare ASA grafted

powder particles. The detailed formulation is summarized in Supplementary Table 1. A certain amount of PBA latex, SDS, and CHP, as well as a reducing agent aqueous solution (I), were added into a 2L three-necked flask, with a constant water bath temperature of 40 °C. After reacting for half an hour, the shell pre-emulsion was added dropwise into the three-necked flask using a peristaltic pump, completing the addition within 3 hours. When 50% of the feeding was complete, the reducing agent aqueous solution (II) was added, and at the end of the continuous feeding, the reducing agent aqueous solution (III) was added. Then, the water bath temperature was adjusted to 65 °C, and the reaction continued for another three hours. Finally, the ASA latex was poured into a beaker at 80 °C with a stirring speed of 400 rpm, and a MgSO₄ aqueous solution was prepared in the beaker as a demulsifier. Filtration was performed to obtain pure ASA grafted powder particles, which were then dried at 60 °C.

2.3.3 Preparation of SAN/ASA blends

Step 1: Dry the SAN resin and ASA grafted powder particles prepared with five different functional crosslinkers at 80 °C for 24 hours. Mix SAN/ASA uniformly in three different ratios to obtain 15 groups of mixtures. Step 2: Set the temperature of the torque rheometer to 180 °C, the rotor speed to 60 r/min, and the time to 10 minutes. When the temperature of the torque rheometer stabilizes at 180 °C, add the mixture into the torque rheometer for melt blending to obtain ASA/SAN blends. Step 3: Label the blends and use 60 mm × 120 mm × 4 mm and 60 mm × 120 mm × 1 mm molds to perform hot pressing on a flat vulcanizing machine, with the machine set at 200 °C and 6 MPa. After cooling, demold to obtain ASA sheets. The detailed experimental process

is shown in Figure 2.

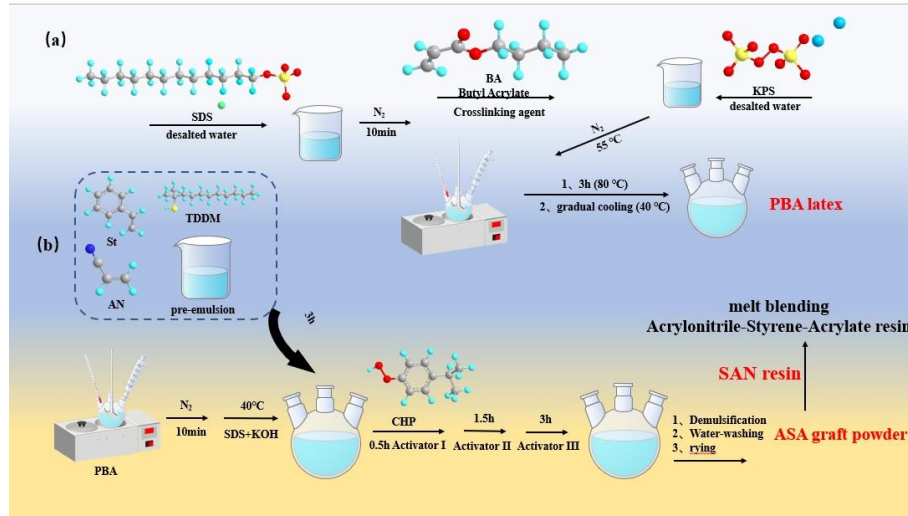


Figure 2 Experimental procedure for the preparation of SAN/ASA blends

2.4 Property testing and characterization

2.4.1 Determination of conversion rate and crosslinking degree

The conversion degree of the reaction monomers was determined using the gravimetric method. The solid content of the experimental formulation was 26%. Based on the polymerization formulation, the total mass of all substances in the reaction system (W_0), the total mass of the monomers participating in the reaction (W_m), and the total mass of non-volatile substances in the reaction system excluding the monomers (W_N) were calculated. Subsequently, a certain amount of PBA latex (W_1) was weighed, placed in a glass container wrapped with aluminum foil, and dried at 60 °C. After drying, it was weighed again (W_2). The conversion rate for each emulsion polymerization was calculated according to the following formula (1).

$$\text{conversion} = \left\{ \frac{W_2}{W_1 \times \frac{W_N}{W_0}} - \frac{W_N}{W_m} \right\} \times 100\% \quad (1)$$

The crosslinking degree of the PBA seed latex was determined using the swelling

method. The dried PBA seed latex film was cut into small pieces of 2 mm × 2 mm, and the initial mass of the sample (m_0) was recorded. The samples were then immersed in three solvents (toluene, chloroform, and tetrahydrofuran) for swelling. The mass of the samples was measured at 12 h intervals until a constant mass was achieved, and the mass at swelling equilibrium (m_e) was recorded. The swelling ratio (Q) was calculated using Equation (2), and the crosslinking degree (D) was calculated using Equation (3).

$$Q = \frac{m_e - m_0}{m_0} \times 100\% \quad (2)$$

$$D = \left(1 - \frac{1}{Q}\right) \times 100\% \quad (3)$$

2.4.2 Particle size and size distribution

The particle size, size distribution width, and polydispersity index (PDI) of the PBA seed latex were determined using a dynamic light scattering (DLS) method with a particle size analyzer (90Plus, Brookhaven, USA). The sample was dropped into a cuvette and diluted with deionized water until it became transparent, after which the particle size and size distribution were measured.

2.4.3 Fourier Transform Infrared Spectroscopy Analysis of ASA grafted powder particles

The chemical structure of the samples was characterized using a Fourier transform infrared spectrometer (INVENIO-R, Bruker, Germany) in attenuated total reflection (ATR) mode with a diamond crystal. The specific test parameters were set as follows: wavenumber range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1} .

2.4.4 Glass transition temperature (T_g)

The glass transition temperature (T_g) of the samples was determined using

differential scanning calorimetry (DSC, FBS-DSC300A, FBS Testing Equipment Co., Ltd., Xiamen, China). The specific test parameters were set as follows: a heating rate of 20 °C/min under a nitrogen atmosphere, a scanning temperature range of -80 °C to 180 °C, and a test duration of 65min.

2.4.5 Determination of grafting ratio and grafting efficiency of ASA graft powder

The grafting ratio of the ASA graft powder samples was determined using the centrifugal separation method. The specific procedure was as follows: First, approximately 1 g of the ASA graft powder sample (W_0) was weighed and added to 20 mL of acetone (a good solvent for free SAN but a non-solvent for ASA grafted core-shell particles). The mixture was magnetically stirred at 25 °C for 30 min to ensure complete dissolution of the ungrafted free SAN. Second, the mixture was centrifuged at 15,000 r/min for 15 min in a high-speed centrifuge to completely sediment the insoluble ASA grafted core-shell particles. The supernatant containing the dissolved free SAN was carefully decanted. The precipitate was collected and dried under vacuum at 40 °C to a constant weight (W_1). The grafting ratio and grafting efficiency were calculated using Equations (4) and (5), where W_{core} represents the mass fraction of the PBA rubber core in the ASA particles (calculated from the PBA feed amount and conversion rate during the preparation process).

$$GD = \frac{W_1 - W_0 \times W_{core}}{W_0 \times W_{core}} \times 100\% \quad (4)$$

$$GE = \frac{W_1 - W_0 \times W_{core}}{W_0 \times (1 - W_{core})} \times 100\% \quad (5)$$

2.4.6 Mechanical property testing

Impact Property Test: Sheets were prepared using a compression molding machine

and processed into standard V-notched specimens. After removing burrs, the specimens were conditioned at 25 °C (room temperature) for 24 h. The notched impact strength at room temperature was tested according to the GB/T 1043-1993 standard using a cantilever beam impact testing machine. Tensile Property Test: Tensile properties were determined according to the GB/T 1040-1992 standard using an electronic universal testing machine at a tensile speed of 50 mm/min and a temperature of 23 °C.

2.4.7 Scanning electron microscopy analysis of ASA resin notched impact specimen morphology

The morphology of the fracture surface of the ASA resin notched impact specimens was observed using a scanning electron microscope (SEM, JSM-6510, Japan). Prior to observation, the fracture surface was sputter-coated with a thin conductive layer of gold.

3 Results and Discussion

3.1 PBA seed latexes prepared with different crosslinking agents

Table 1 List of PBA seed latexes

Sample	Crosslinker type	Crosslinker dosage (wt%)	Emulsifier dosage (wt%)	Initiator dosage (wt%)	PDI
PBA-C1	DCPA	2	0.38	0.2	0.026
PBA-C2	MBA	2	0.38	0.2	0.049
PBA-C3	EGDMA	2	0.38	0.2	0.026
PBA-C4	DMA	2	0.38	0.2	0.003
PBA-C5	PETA	2	0.38	0.2	0.047

3.2 ASA graft powders prepared with different crosslinking agents

In the experiment, an initiator content of 0.2 wt% was found to be optimal, offering a favorable balance between effectiveness and production cost. Therefore, in the preparation of ASA graft powders with different crosslinking agents, the initiator content was fixed at 0.2 wt%, the emulsifier content at 0.38 wt%, and the crosslinking agent content at 2 wt%. Five crosslinking agents were primarily selected for this study, namely diallyl phthalate (DCPA), N, N'-methylenebisacrylamide (MBA), ethylene glycol dimethacrylate (EGDMA), N, N'-dimethylacrylamide (DMA), and pentaerythritol triacrylate (PETA).

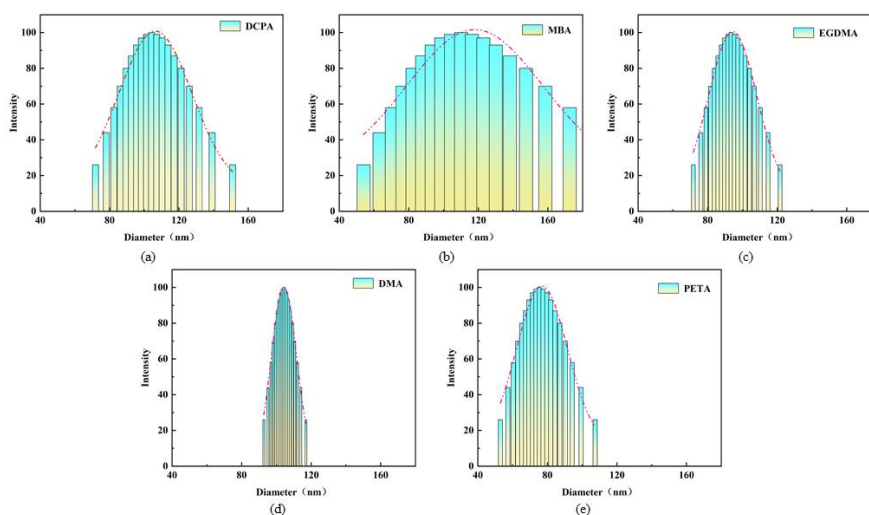


Figure 3 Particle size distribution of PBA seed latexes prepared with different crosslinking agents: (a) PBA-C1, (b) PBA-C2, (c) PBA-C3, (d) PBA-C4, (e) PBA-C5

Based on the data presented in Table 1 and Fig. 3, it can be observed that, except the PETA-crosslinked latex which exhibited a relatively smaller particle size, the particle sizes of the PBA latexes prepared with the other four crosslinking agents were generally in the range of 100-110 nm. Among these, the PBA latex prepared with DMA displayed the narrowest particle size distribution and uniform nucleation, which is conducive to the formation of core-shell ASA graft particles with good dispersion and

uniform structure. In contrast, the PBA latex prepared with MBA showed the broadest particle size distribution, which may lead to poor colloidal stability and a tendency for particle agglomeration or structural defects during the grafting process. Therefore, based on the particle size analysis, the DMA-crosslinked PBA latex exhibits superior application potential for the subsequent preparation of ASA graft powders and can be prioritized as the seed latex.

Table 2 Crosslinking degree of PBA seed latexes in different solvents

Sample	Crosslinker type	Crosslinker dosage (wt%)	Toluene (%)	Chloroform (%)	Tetrahydrofuran (%)
PBA-C1	DCPA	2	89.58	94.04	87.79
PBA-C2	MBA	2	89.14	93.91	87.46
PBA-C3	EGDMA	2	87.69	91.87	87.73
PBA-C4	DMA	2	89.99	94.48	87.38
PBA-C5	PETA	2	90.23	96.23	88.21

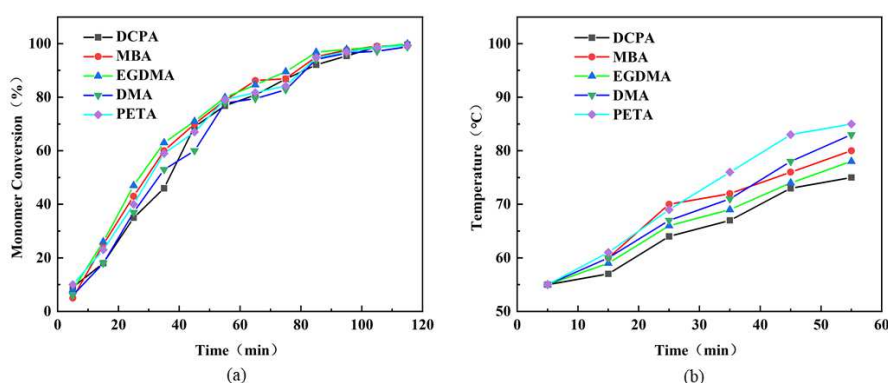


Figure 4 (a) Conversion and (b) peak temperature

Based on the analysis of the data in Table 2 and Fig. 4, it can be seen that the maximum conversion rates for all five crosslinking agents reached approximately 99%, while the crosslinking degree showed an increasing trend. This phenomenon can be attributed to the increase in system viscosity, which enhances the Trommsdorff effect (auto-acceleration effect), hindering the diffusion of free radicals and consequently leading to an increase in polymerization rate and exothermic intensity. The crosslinking

agent DCPA significantly reduced both the polymerization rate and exothermic intensity. In contrast, the crosslinking agent PETA exhibited the highest peak temperature. This is because PETA molecules tend to form a three-dimensional crosslinked network easily in the early stages of the reaction. Once the reaction enters the gelation stage, the system viscosity increases sharply, severely restricting the diffusion of chain segments and free radicals, resulting in a dramatic increase in polymerization rate and exothermic intensity. Meanwhile, DMA, due to the relatively low activity of its allyl groups, exhibited a polymerization rate and peak temperature intermediate between those of DCPA and PETA.

3.2.1 FTIR analysis of ASA graft powders synthesized with five crosslinking agents

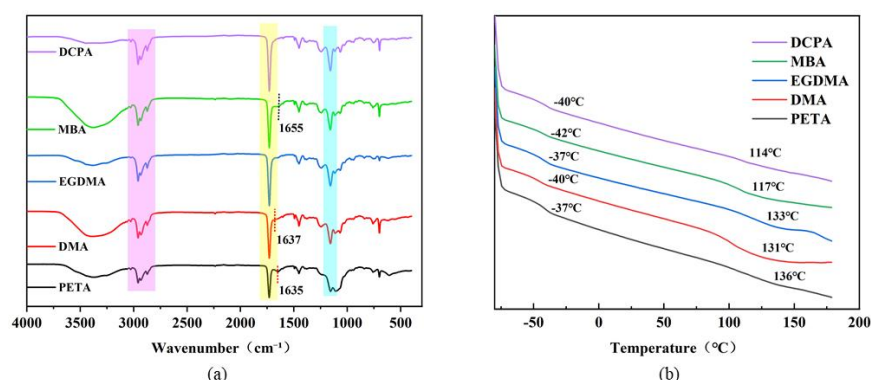


Figure 5 (a) FTIR spectra of ASA graft powders synthesized with five crosslinking agents and (b) DSC curves of ASA graft powders synthesized with five crosslinking agents

As shown in Fig. 5(a), the successful preparation of the ASA graft powder samples was confirmed by Fourier transform infrared spectroscopy (FTIR), which characterized the functional group structures of the five samples in the range of 500-4000 cm^{-1} . The absorption band around 3000 cm^{-1} was attributed to the superimposed stretching vibrations of C-H bonds in the benzene ring and alkyl groups. The strong absorption peak at 1730 cm^{-1} , corresponding to C=O stretching vibration, confirmed the presence

of the PBA core. The intense stretching vibration peak of the ester C-O single bond originating from the crosslinking agents was observed at approximately 1100 cm^{-1} . The intensity of the residual C=C stretching vibration peak at 1635 cm^{-1} decreased in the order of PETA > DMA > MBA > EGDMA.

As shown in Fig. 5(b), analysis of the DSC data indicated the successful synthesis of ASA graft powder with a core-shell structure. The low-temperature T_g corresponded to the glass transition of the PBA rubber phase, while the high-temperature T_g corresponded to the glass transition of the rigid SAN phase. The low-temperature T_g of all samples was concentrated in the range of $-37\text{ }^{\circ}\text{C}$ to $-42\text{ }^{\circ}\text{C}$, suggesting that the crosslinking agent had little influence on the rubber phase, thereby maintaining good low-temperature toughness. However, the high-temperature T_g of the rigid SAN phase exhibited significant differences. The T_g values for samples prepared with PETA, DMA, and EGDMA were higher, all exceeding $130\text{ }^{\circ}\text{C}$, while those for MBA and DCPA were only around $110\text{ }^{\circ}\text{C}$.

3.3 Effect of ASA graft powders prepared with different crosslinking agents on the toughening of SAN resin

3.3.1 Analysis of grafting ratio of ASA graft polymers prepared with different crosslinking agents

Table 3 Grafting ratio of ASA graft polymers prepared with different crosslinking agents

Sample	Crosslinker type	Crosslinker dosage (wt%)	Diameter (nm)	Grafting degree (%)
ASA-C1	DCPA	2	104.1	30.1
ASA-C2	MBA	2	106.2	32.6
ASA-C3	EGDMA	2	106.8	30.7
ASA-C4	DMA	2	106.0	34.6

ASA-C5	PETA	2	99.3	29.4
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Analysis of the data in Table 3 reveals that DMA exhibited the highest grafting ratio of 34.6%. This is attributed to the strong electron-donating ability of the tertiary amino group ($-\text{N}(\text{CH}_3)_2$) in its molecular structure, which can form charge interactions with ASA, thereby improving the grafting efficiency. MBA also showed a relatively high grafting ratio of 32.6%, which can be explained by the hydrogen bonding interactions between its bisamide structure and the nitrile groups ($-\text{CN}$) in ASA, enhancing interfacial compatibility. In contrast, PETA exhibited the lowest grafting ratio of 29.4%. This is because its three-dimensional network structure increases steric hindrance, which reduces the reaction activity for grafting.

3.3.2 Analysis of mechanical properties of SAN/ASA blends with different ratios

To investigate in more detail the effect of ASA content on the toughening of SAN resin, the mass ratio of styrene (St) to acrylonitrile (AN) was fixed at 3:1. This monomer mixture was grafted onto PBA cores prepared with different crosslinking agents, yielding five types of ASA graft powders. Subsequently, SAN and ASA were blended in three mass ratios (40/20, 35/25, and 30/30) to compare the combined effects of the crosslinking agent type and the SAN/ASA ratio on the mechanical properties of the resulting blends.

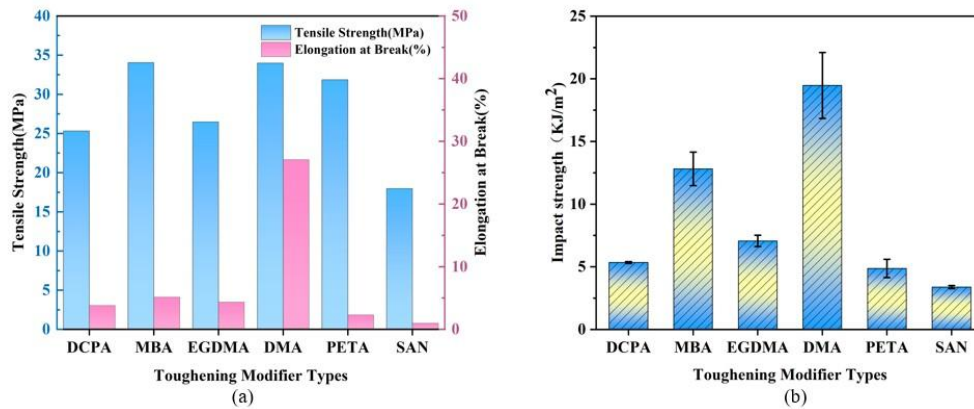


Figure 6 (a) Tensile strength and elongation at break of SAN/ASA (40/20) blends with different crosslinking agents, (b) Notched Izod impact strength

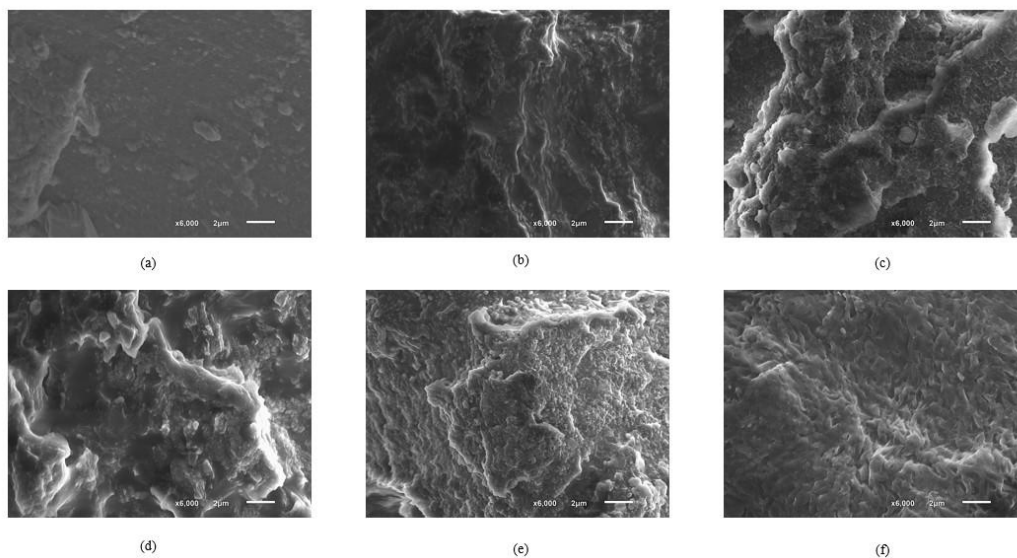


Figure 7 SEM images of notched impact fracture surfaces of SAN/ASA (40/20) blends prepared with different crosslinking agents: (a) neat SAN, (b) DCPA, (c) MBA, (d) EGDMA, (e) DMA, and (f) PETA. The scale bar represents 2 μm .

Firstly, the tensile strength, elongation at break, and notched impact strength of the blends were tested and analyzed with a fixed SAN/ASA mass ratio of 40/20. The results presented in Fig. 6(a) show that the neat SAN resin exhibited a tensile strength of 17.97 MPa and an elongation at break of 0.97%. Upon incorporation of 20 g of ASA particles, both the tensile strength and elongation at break of all samples increased to varying degrees. The most significant improvement was observed for the sample containing

ASA particles prepared with DMA, which achieved a tensile strength of 33.98 MPa and an elongation at break of 27.06%. The samples containing ASA particles prepared with PETA and MBA exhibited tensile strengths of 31.86 MPa and 34.05 MPa, respectively, but their elongation at break was only 2.31% and 5.14%, respectively. The results presented in Fig. 6(b) indicate that the notched impact strength of neat SAN resin was only 3.38 kJ/m², characteristic of typical brittle fracture. After the addition of ASA particles, the impact strength also increased to varying degrees. The sample containing ASA particles prepared with DMA exhibited the greatest improvement in impact toughness, reaching 19.47 kJ/m², which is a six-fold increase compared to neat SAN resin. The sample containing ASA particles prepared with MBA achieved an impact strength of 12.83 kJ/m², a four-fold increase. However, the impact strength of the sample containing ASA particles prepared with PETA was only 4.87 kJ/m². These results suggest that the DMA crosslinking agent can generate a more efficient stress transfer network, effectively inducing a synergistic toughening mechanism involving matrix shear yielding and crazing. In contrast, the crosslinking agents DCPA and PETA impose insufficient constraints on the deformability of the rubber particles, causing the particles to be prone to premature fracture under impact loading. The above analysis leads to the conclusion that, in the SAN/ASA (40/20) blend system, the use of the DMA crosslinking agent achieves the maximum improvement in impact toughness while simultaneously enhancing tensile strength.

The notched impact fracture surfaces of SAN/ASA (40/20) blends prepared with different crosslinking agents were examined by scanning electron microscopy (SEM),

as shown in Fig. 7. The results revealed that the fracture surface of neat SAN resin was smooth and flat, with linear crack propagation, characteristic of brittle fracture. Upon incorporation of ASA particles, all fracture surfaces became rougher, exhibiting deformation and the formation of void structures. Specifically, Fig. 7(b) shows a slightly rough surface. In Figs. 7(c) and (d), not only roughness but also pronounced tearing marks and a partially fibrous appearance were observed. Fig. 7(e) displays the roughest fracture surface, characterized by numerous and uniformly distributed voids, which is distinctly different from the others and indicative of ductile fracture. In contrast, Fig. 7(f) shows a fracture surface with less deformation, exhibiting a honeycomb-like structure and extensive crack bifurcation. Based on the above analysis, the reasons for these differences can be elucidated. The honeycomb structure observed for PETA reflects excessive crosslinking, leading to increased brittleness. The ductile texture observed for DMA and the crazing fracture observed for MBA corresponded well with their high impact strengths. Therefore, the DMA crosslinking agent achieved an optimal balance between crosslinking density and mechanical properties.

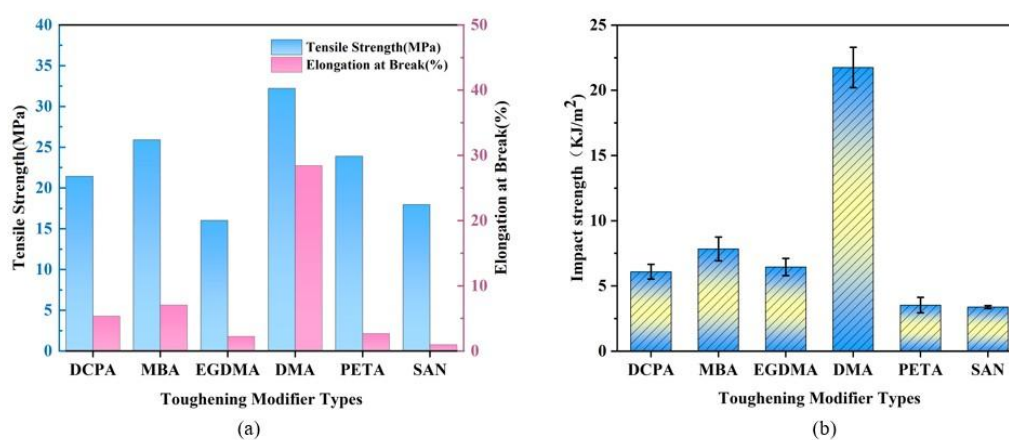


Figure 8 (a) Tensile strength and elongation at break of SAN/ASA (35/25) blends with different crosslinking agents, (b) Notched Izod impact strength

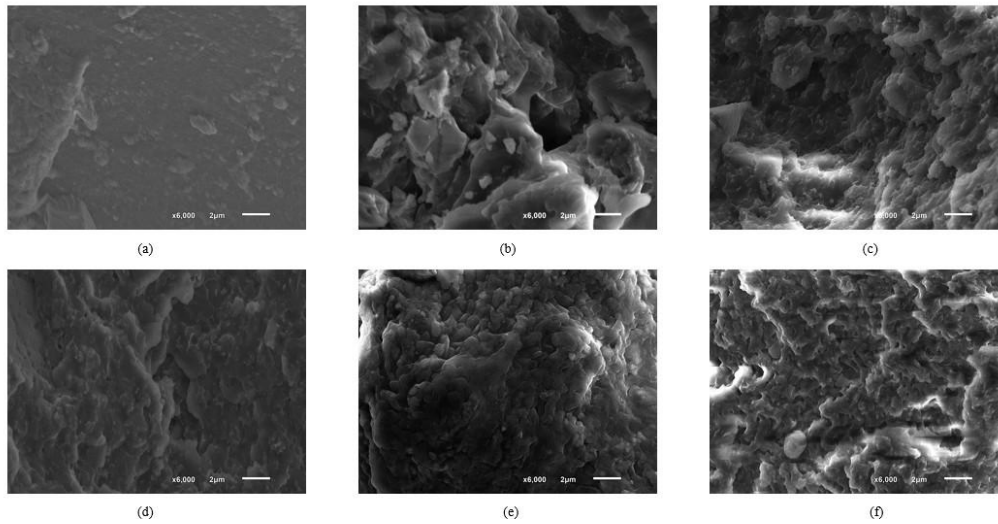


Figure 9 SEM images of notched impact fracture surfaces of SAN/ASA (35/25) blends prepared with different crosslinking agents: (a) neat SAN, (b) DCPA, (c) MBA, (d) EGDMA, (e) DMA, and (f) PETA. The scale bar represents 2 μm .

As shown in Fig. 8, in this blend system, with a fixed SAN/ASA mass ratio of 35/25, the incorporation of ASA particles prepared with DMA increased the tensile strength to 32.23 MPa. The elongation at break (28.44%) was higher than that of the SAN/ASA (40/20) blend, and the impact strength also increased to 21.7 kJ/m². This indicates that the ASA particles prepared with DMA exhibit superior performance in the SAN/ASA (35/25) blend system. Analysis of the SEM image in Fig. 9(e) reveals a surface characterized by densely distributed nodular protrusions, which are microdomain structures formed by the aggregation of crosslinking points. This rough surface morphology facilitates stress distribution. The high-density network formed by the DMA crosslinking agent significantly induces matrix deformation, demonstrating optimal impact toughness. A more pronounced difference compared to Fig. 7 is observed in Fig. 9(b), where the fracture surface exhibits a layered fragment structure. In this case, the distribution of crosslinking points leads to stress concentration,

triggering localized layer delamination. This morphology reflects the insufficient compatibility between the crosslinked network formed by the ASA particles prepared with DCPA and the matrix in this blend system. At this blending ratio, the tensile and impact properties of the other blends containing ASA particles decreased compared to those of the SAN/ASA (40/20) blend system.

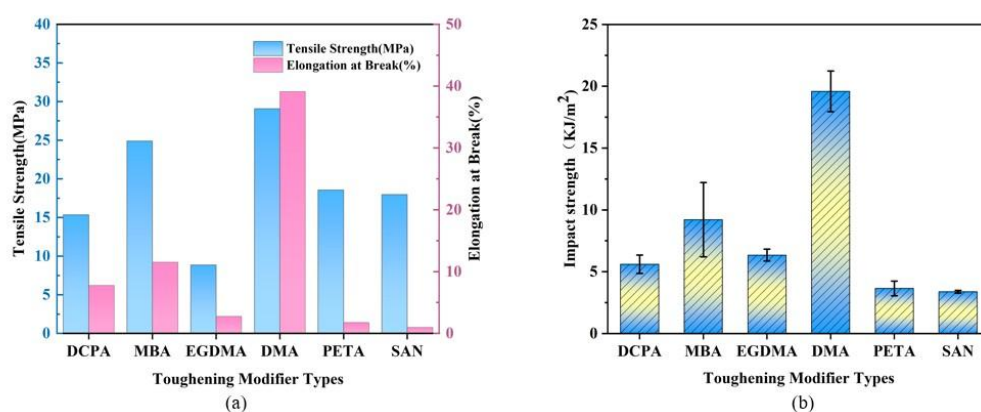


Figure 10 (a) Tensile strength and elongation at break of SAN/ASA (30/30) blends with different crosslinking agents, (b) Notched Izod impact strength

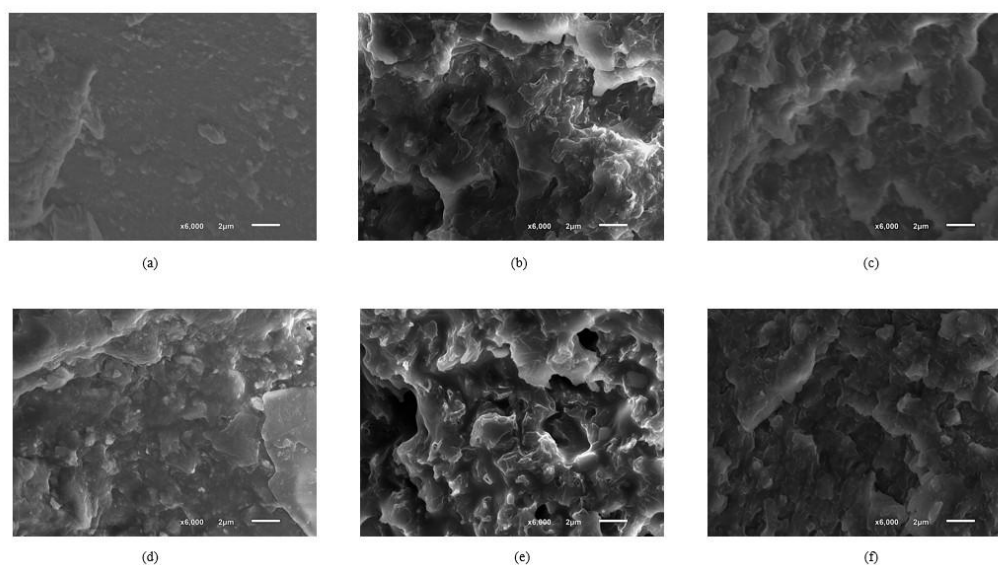


Figure 11 SEM images of notched impact fracture surfaces of SAN/ASA (30/30) blends prepared with different crosslinking agents: (a) neat SAN, (b) DCPA, (c) MBA, (d) EGDMA, (e) DMA, and (f) PETA. The scale bar represents 2 μm.

In this blend system, with a fixed SAN/ASA mass ratio of 30/30, analysis of Fig.

10 reveals that, compared to the SAN/ASA (40/20) system, the tensile strengths of blends prepared with the same series of crosslinking agents decreased significantly, while their elongations at break increased substantially. Specifically, the tensile strength of blends containing ASA particles prepared with DCPA, MBA, EGDMA, and PETA decreased by a minimum of 10 MPa and a maximum of 18 MPa. However, their elongations at break increased by up to 50% compared to the SAN/ASA (40/20) system. This phenomenon can be primarily attributed to the following reasons. In the SAN/ASA (40/20) blend system, the higher SAN content results in a higher overall modulus and consequently higher tensile strength. However, due to the relatively low proportion of ASA particles, the overall toughness is somewhat limited: the interfacial area between phases is relatively sparse, leading to a lower elongation at break compared to the SAN/ASA (30/30) blend system. In contrast, in the SAN/ASA (30/30) blend system, the comparable ASA content allows its flexible chains to disperse within the SAN matrix, forming a better phase dispersion structure. Although the tensile strength derived from SAN is compromised, the shearing and dispersing effects of the ASA particles significantly enhance the overall toughness, resulting in a marked increase in elongation at break.

Examination of the impact fracture surfaces of SAN/ASA (30/30) blends by scanning electron microscopy (SEM) in Fig. 11 reveals a more pronounced lamellar structure compared to the previous two blend systems. In the SAN/ASA (40/20) blend system, impact energy is dissipated by initiating crazing and shear yielding within the SAN matrix. The rubber particles act as stress concentrators, terminating a large number

of micro-crazes. The resulting fracture morphology, as shown in Fig. 7, is characterized by a ductile undulating structure composed of relatively uniform micro-voids. In contrast, in the SAN/ASA (30/30) blend system, where the ASA content is comparable to that of SAN, the system tends to form a co-continuous structure rather than a simple “sea-island” morphology. This structure generates a large interfacial area between the two phases. When impact stress is applied to the material, it is transferred and concentrated along these continuous phase interfaces. Due to the significant modulus mismatch between the SAN and ASA phases, layer-by-layer tearing occurs under high-speed impact, analogous to peeling apart a stack of paper. This results in the distinct lamellar or sheet-like structures observed in the SEM images for samples prepared with various crosslinking agents, as shown in Figs. 11(b), (d), (e), and (f). A more extensive and developed lamellar structure indicates greater energy absorption before fracture, signifying improved toughness. This observation correlates well with the increased elongation at break values observed for all samples in the SAN/ASA (30/30) blend system.

4 Conclusions

The experimental results demonstrate that all five crosslinking agents provide effective reaction sites for the grafting of the SAN shell onto the PBA core, albeit with variations in grafting ratio and toughening efficiency for the SAN resin. Among them, DMA exhibited the highest grafting ratio, reaching 34.6%. The ASA graft powder prepared with DMA, when incorporated into the SAN/ASA (35/25) blend system, showed optimal comprehensive mechanical properties, with the notched impact

strength increased to 21.7 kJ/m² and an elongation at break of 28.44%, significantly outperforming the other crosslinking agents. SEM analysis revealed a rough fracture surface with abundant voids for this blend, characteristic of typical ductile fracture, indicating that the structure of the crosslinking agent significantly influences the deformability of the rubber particles and the energy dissipation mechanism during fracture. This study systematically compares the effects of different crosslinking agents on the structure of ASA and its toughening performance in SAN blends, providing an experimental basis and reference for the formulation design and industrial application of high-performance ASA resins.

Statements and Declarations:

Competing Interests: The author declares that there are no financial and non-financial conflicts of interest.

Acknowledgments: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Author contributions: **Xu Wenyu:** Validation, Data curation, Writing – review & editing, Software. **Li Yan, Yan Zhixiang:** Background research, Bibliographic search.

Huang Jiaheng: investigation **Zhiyong Tan:** Funding acquisition, Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization.

Data and code availability: Some or all data, models, or code generated or used during the study are available in a repository or online in accordance with funder data retention policies (Provide full citations that include URLs or DOIs.)

Supplementary information: No supplementary information is included in the paper.

Ethical approval: No experiments involving animals or human tissues were conducted in this study.

Declaration of interests

The author declares that there are no financial and non-financial conflicts of interest.

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