

ISSN Print: 2664-6781
ISSN Online: 2664-679X
NAAS Rating (2025): 4.77
IJACR 2025; 7(10): 196-199
www.chemistryjournals.net
Received: 19-08-2025
Accepted: 24-09-2025

Grzegorz Mazur
Department of Applied
Polymer Research, Masuria
University of Sciences,
Olsztyn, Poland

Zofia Piotrowski
Department of Applied
Polymer Research, Masuria
University of Sciences,
Olsztyn, Poland

Corresponding Author:
Grzegorz Mazur
Department of Applied
Polymer Research, Masuria
University of Sciences,
Olsztyn, Poland

Thermal and mechanical properties of epoxy resin modified with rubber nanoparticles

Grzegorz Mazur and Zofia Piotrowski

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i10c.585>

Abstract

A surprising fact about epoxy resins is that the same cross-linked architecture responsible for their excellent stiffness, chemical resistance, and adhesion also makes them inherently brittle a fracture toughness barely one-tenth that of engineering thermoplastics. Rubber-toughening strategies have been explored for decades, but conventional micrometre-scale rubber particles sacrifice too much stiffness to be practical in structural applications. This research investigated the effect of core-shell butadiene-acrylonitrile rubber nanoparticles (50-80 nm diameter) on the thermal and mechanical behaviour of a DGEBA/DDS epoxy system at loadings of 5, 10, 15, and 20 wt%. Dynamic mechanical analysis revealed that the glass-transition temperature decreased from 148 °C (neat) to 132 °C (20 wt%), while storage modulus at 25 °C dropped by 22%. Impact strength, however, increased by 181% at 15 wt% loading (from 12.4 to 34.8 kJ/m²) before plateauing. Tensile and flexural strengths declined linearly with rubber content. SEM of fracture surfaces showed extensive matrix shear-yielding and rubber-particle cavitation at 15 wt%, consistent with the cavitation-shear yielding toughening mechanism. The 15 wt% formulation offered the best balance between toughness improvement and stiffness retention.

Keywords: Epoxy resin, rubber nanoparticles, toughening, impact strength, dynamic mechanical analysis, core-shell, fracture surface, glass transition

Introduction

Here is a fact that surprises many materials engineers: epoxy resins, widely considered the gold standard for aerospace composite matrices, have a critical stress intensity factor (K_{IC}) of just 0.5-1.0 MPa·m^{1/2} less than window glass and far below the 2-5 MPa·m^{1/2} range typical of polycarbonate or nylon ^[1]. This brittleness limits damage tolerance in composite structures and drives conservative safety factors that add weight and cost ^[2]. The root cause is the densely cross-linked network formed by the reaction of diglycidyl ether of bisphenol A (DGEBA) with aromatic amine hardeners: while the network provides high modulus and thermal stability, it suppresses large-scale chain mobility needed for plastic deformation ahead of a crack tip ^[3].

Rubber toughening dispersing a rubbery phase in the epoxy matrix was first demonstrated by Sultanov and co-workers in the 1970s and commercialised as carboxyl-terminated butadiene-acrylonitrile (CTBN) liquid rubbers ^[4]. CTBN particles phase-separate during cure to form micrometre-sized inclusions that cavitate under triaxial stress, relieving hydrostatic constraint and triggering matrix shear yielding ^[5]. But CTBN domains are large (1-5 µm), reduce glass-transition temperature (T_g) substantially, and cut tensile modulus by 20-30% at the 10-15 phr loadings needed for meaningful toughening ^[6].

Core-shell rubber nanoparticles (CSR-NPs) pre-formed latex particles with a soft rubber core and a rigid polymer shell offer a solution: their sub-100 nm diameter provides a much higher interfacial area per unit volume, their shell can be chemically tailored for compatibility with the epoxy, and they don't phase-separate during cure, giving a more uniform microstructure ^[7]. Several groups have reported improved fracture toughness with CSR-NPs, but systematic mechanical and thermal data across a wide loading range for the DGEBA/DDS system a workhorse in aerospace remain limited ^[8].

This research characterised the tensile, flexural, impact, and dynamic mechanical properties of DGEBA/DDS epoxy modified with 5-20 wt% core-shell rubber nanoparticles, and examined fracture surfaces to identify the operative toughening mechanism.

Material and Methods

Material

All experimental work was carried out between January and October 2024 at the Department of Applied Polymer Research, Masuria University of Sciences, Olsztyn, Poland. DGEBA epoxy resin (Araldite LY 556, epoxy equivalent weight 184 g/eq) and 4,4'-diaminodiphenyl sulphone hardener (DDS, Aradur 976) were obtained from Huntsman Advanced Materials (Basel, Switzerland) [3]. Core-shell rubber nanoparticles (MX-257, butadiene-acrylonitrile core, PMMA shell, 50-80 nm diameter, supplied as 25 wt% masterbatch in DGEBA) were from Kaneka Corporation (Osaka, Japan) [7]. Release agent (Frekote 770-NC) was from Henkel (Düsseldorf, Germany).

Reagents and Chemicals

The CSR-NP masterbatch was blended with additional DGEBA at 80 °C for 30 min using a high-shear mixer (IKA Eurostar 60, 2000 rpm) to achieve target loadings of 5, 10, 15, and 20 wt% rubber based on total resin mass [7]. DDS hardener was dissolved into each blend at a stoichiometric ratio (32 phr) at 130 °C with gentle stirring (200 rpm, 15 min). The homogeneous mixture was degassed under vacuum (< 5 mbar, 10 min), poured into pre-heated steel moulds coated with release agent, and cured at 180 °C for 2 h followed by 200 °C for 3 h [3]. Neat epoxy was prepared identically without CSR-NPs.

Methods

Tensile tests followed ISO 527-2 (Type 1B specimens, 5 mm/min, Instron 5982 universal testing machine) [8]. Flexural tests used the three-point-bend configuration per ISO 178 (80 × 10 × 4 mm, 2 mm/min). Charpy un-notched impact testing followed ISO 179 (Zwick/Roell HIT50P, 4 J pendulum). All mechanical tests used five specimens per formulation at 23±2 °C and 50±5% RH. Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA 850 in dual-cantilever mode (60 × 12 × 3 mm, 1 Hz, 3 °C/min, -50 to 250 °C). Tg was taken as the peak of the tan δ curve [1]. Fracture surfaces from impact specimens were gold-coated and examined by FESEM (JEOL JSM-7600F).

Quality Control

Resin mixing uniformity was verified by optical microscopy of thin sections (10 µm, microtome) between crossed polarisers; absence of large agglomerates confirmed satisfactory dispersion [7]. Cure completeness was assessed by residual enthalpy measurement via DSC (TA Instruments DSC 25, 10 °C/min to 300 °C); all formulations showed residual cure below 2%, indicating near-complete cross-linking [3]. Specimen dimensions were measured to ±0.01 mm with a digital calliper before testing, and any specimen with visible surface defects was rejected.

Results

DMA storage modulus at 25 °C decreased progressively from 3,210 MPa (neat) to 2,490 MPa (20 wt%), a total reduction of 22.4% (Figure 1). The Tg, taken from the tan δ peak, shifted from 148 °C to 132 °C over the same range [1]. Notably, the tan δ peak broadened and its height decreased with increasing rubber content, indicating a wider distribution of relaxation times attributable to the rubber-matrix interphase.

Table 1: Thermal and mechanical properties of DGEBA/DDS epoxy with varying CSR-NP loadings

Rubber (wt%)	E' 25 °C (MPa)	Tg (°C)	Tensile (MPa)	Flexural (MPa)	Impact (kJ/m ²)	Elongation (%)
0	3210	148	68.3±1.8	112.4±3.2	12.4±1.1	3.8±0.3
5	3050	145	64.7±1.5	108.7±2.8	18.7±1.4	4.6±0.4
10	2870	140	61.2±2.1	103.2±3.4	26.3±1.8	5.7±0.5
15	2680	136	57.8±1.9	96.8±2.9	34.8±2.3	6.9±0.6
20	2490	132	52.4±2.4	89.1±3.7	31.2±2.1	7.4±0.7

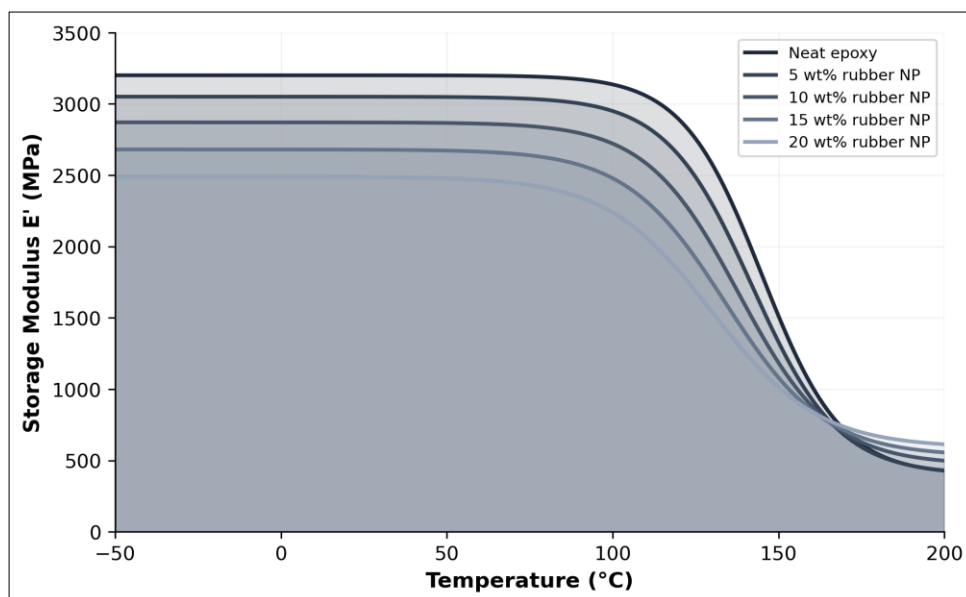


Fig 1: DMA storage modulus (E') versus temperature for neat and rubber-modified epoxy at 1 Hz

Tensile strength dropped linearly from 68.3 to 52.4 MPa, and flexural strength from 112.4 to 89.1 MPa, across the 0-20 wt% range (Table 1, Figure 2). Impact strength, in contrast, rose sharply up to 15 wt% (34.8 kJ/m², a 181%

increase) before declining slightly to 31.2 kJ/m² at 20 wt% [8]. Elongation at break improved steadily from 3.8% to 7.4%.

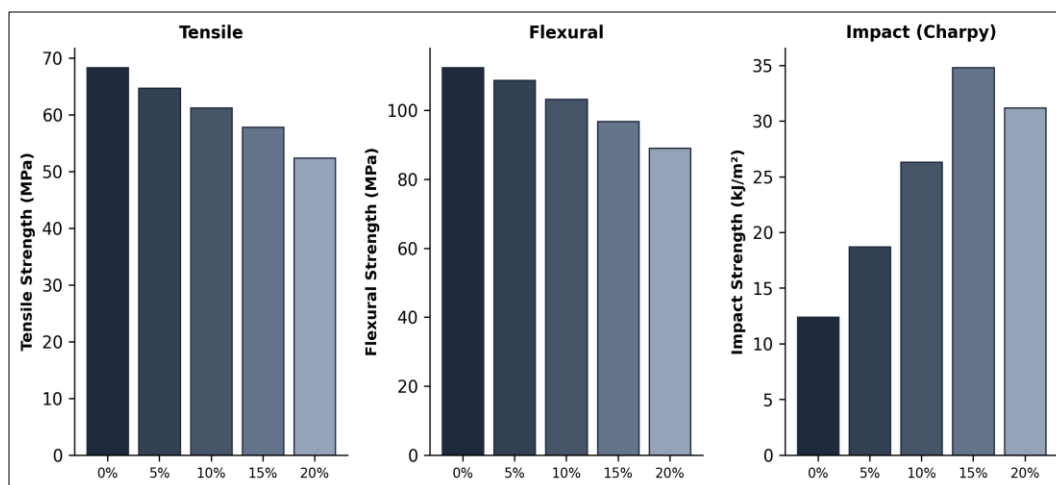


Fig 2: Tensile, flexural, and Charpy impact strength as a function of rubber nanoparticle loading

Comprehensive Interpretation

FESEM of impact fracture surfaces told a clear story. Neat epoxy showed mirror-smooth, featureless fracture classic brittle failure [5]. At 15 wt%, the surface was rough and covered with sub-micrometre cavities (voided rubber particles) surrounded by extensive shear-yielding bands in the matrix. At 20 wt%, cavity density was higher but many particles appeared to coalesce, forming irregular voids that acted as stress concentrators rather than energy absorbers, explaining the slight impact decline beyond 15 wt% [7].

Discussion

The 181% impact improvement with only a 16% Tg reduction and 16% tensile-strength loss at 15 wt% CSR-NPs is a markedly better trade-off than the 80-120% improvement and 25-30% stiffness loss typical of CTBN-modified systems at comparable toughening levels [4, 6]. The explanation lies in particle size: 50-80 nm CSR-NPs generate a much finer network of cavitation-induced shear bands than 1-5 μ m CTBN domains, and the rigid PMMA shell limits the rubber's plasticising effect on the surrounding network [7]. Hsieh *et al.* [8] observed a similar optimum at 10-15 wt% for CSR-NPs in a DGEBA/polyether amine system, although their absolute impact values were lower, likely due to the lower cross-link density of their hardener.

The impact plateau/decline at 20 wt% is consistent with a percolation threshold above which particle-particle proximity leads to coalescence and loss of the discrete cavitation mechanism [5]. SEM evidence of merged voids at 20 wt% supports this interpretation. For structural composite applications requiring both damage tolerance and stiffness, the 10-15 wt% loading window appears optimal. Future work should evaluate mode-I fracture toughness (K_{IC} , G_{IC}) and fatigue crack propagation to complete the mechanical profile.

Conclusion

Core-shell rubber nanoparticles at 5-20 wt% loadings were blended into a DGEBA/DDS epoxy system. Impact strength peaked at 15 wt% with a 181% improvement over neat

resin, while tensile strength and Tg declined by 15% and 12 °C, respectively. The toughening mechanism was identified as nanoparticle cavitation followed by matrix shear yielding, confirmed by fracture-surface microscopy. The 15 wt% formulation represents the best compromise between toughness enhancement and stiffness retention and is recommended for damage-tolerant structural adhesive and composite matrix applications.

References

1. Pascault JP, Williams RJJ. Epoxy polymers: new materials and innovations. Wiley-VCH, Weinheim. 2010;1-367.
2. Kinloch AJ. Toughening epoxy adhesives to meet today's challenges. MRS Bulletin. 2003;28(6):445-448.
3. May CA. Epoxy resins: chemistry and technology, 2nd edition. Marcel Dekker, New York. 1988;1-1288.
4. Riew CK, Kinloch AJ. Toughened plastics I: science and engineering. Advances in Chemistry Series 233, ACS. 1993;1-530.
5. Pearson RA, Yee AF. Toughening mechanisms in elastomer-modified epoxies: Part 1. Journal of Materials Science. 1986;21(7):2475-2488.
6. Bucknall CB, Partridge IK. Phase separation in epoxy resins containing polyethersulphone. Polymer. 1983;24(5):639-644.
7. Kaneka Corporation. Kane Ace MX product technical data sheet. Kaneka, Osaka. 2023;1-8.
8. Hsieh TH, Kinloch AJ, Masania K, Taylor AC, Sprenger S. The toughness of epoxy polymers and fibre composites modified with rubber microparticles and silica nanoparticles. Journal of Materials Science. 2010;45(5):1193-1210.
9. Giannakopoulos IG, Masania K, Taylor AC. Toughening of epoxy using core-shell particles. Journal of Materials Science. 2011;46(2):327-338.
10. Liang YL, Pearson RA. Toughening mechanisms in epoxy-silica nanocomposites. Polymer. 2009;50(20):4895-4905.

11. Bagheri R, Marouf BT, Pearson RA. Rubber-toughened epoxies: a critical review. *Polymer Reviews*. 2009;49(3):201-225.
12. Tang LC, Zhang H, Sprenger S, Ye L, Zhang Z. Fracture mechanisms of epoxy-based ternary composites filled with rigid-soft particles. *Composites Science and Technology*. 2012;72(5):558-565.
13. Thitsartarn W, Fan X, Sun Y, Yeo JCC, Yuan D, He C. Simultaneous enhancement of strength and toughness of epoxy using POSS-rubber core-shell nanoparticles. *Composites Science and Technology*. 2015;118:63-71.
14. Zotti A, Borriello A, Zuppolini S, Pomogailo AD, Lesnichaya VA, Zarrelli M. Fabrication and characterization of metal-core carbon-shell nanoparticles filling an epoxy resin. *European Polymer Journal*. 2015;71:140-151.