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Crosslinking In Polymers: Fundamentals, Applications, And Optimization

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Abstract

Crosslinking in polymers is a transformative chemical modification that links individual macromolecular chains into a permanent three-dimensional network. This process improves thermal stability, mechanical strength, and chemical resistance, enabling polymers to perform reliably in harsh environments. The present study investigates the effect of different crosslinking agents—silane, dicumyl peroxide (DCP), Triallyl Isocyanurate (TAIC), and Trimethylolpropane Monomethacrylate (TMPMA)—on the structural and mechanical behaviour of polyolefin blends. Both computational and laboratory-scale experiments were conducted using locally sourced materials from Indian suppliers to simulate industrially relevant processing conditions. The optimised formulation containing 1.5 wt% DCP and balanced TAIC + TMPMA co-agents achieved a 27 % rise in gel fraction, 24 % improvement in tensile strength, and 60 °C increase in degradation onset temperature compared with the uncrosslinked polymer. The study highlights that controlled crosslinking not only enhances polymer performance but also contributes to the development of durable, energy-efficient materials suited to India's expanding renewable and infrastructure sectors.

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1. INTRODUCTION

Polymers occupy a central position in modern materials science due to their lightweight, processable, and cost-effective nature. Yet, their relatively low thermal endurance and mechanical strength have long limited their use in demanding applications such as cable insulation, solar encapsulants, and structural composites. Crosslinking has emerged as one of the most versatile strategies for overcoming these deficiencies. By introducing chemical bridges between polymer chains, crosslinking transforms a thermoplastic into a dimensionally stable three-dimensional network capable of withstanding mechanical and thermal stress.

In India, polymer consumption has increased exponentially over the last two decades, driven by rapid industrialisation and renewable-energy initiatives. Studies by Reddy *et al.* (2019) at the Indian Institute of Chemical Technology and Bhattacharya and Singh (2021) from IIT Kharagpur have emphasised the importance of indigenous crosslinking technologies for power-cable insulation and photovoltaic modules. Indian research has also explored hybrid peroxide-silane systems compatible with local climatic conditions, demonstrating that humidity-activated silane curing is particularly suitable for tropical environments where ambient moisture levels facilitate rapid network formation.

Crosslinking mechanisms typically proceed via free-radical reactions initiated by peroxides, condensation of silane-grafted precursors, or reactions with multifunctional co-agents such as TAIC and TMPMA. Each mechanism affects polymer morphology differently. Peroxide-based systems promote rapid network formation but can induce chain scission if overdosed, whereas silane systems generate moisture-curable linkages that enhance long-term stability. Co-agents such as TAIC and TMPMA act as molecular bridges, improving both crosslink density and inter-phase compatibility within polymer blends.

Optimization of these systems requires balancing mechanical integrity with processability. Excessive crosslinking leads to brittleness and reduced elongation, while insufficient linkage density fails to provide adequate dimensional stability. The ideal composition must therefore achieve moderate crosslink density that yields improved tensile strength and thermal resistance without sacrificing flexibility. Indian researchers, notably Nair *et al.* (2022) from CIPET Chennai, have demonstrated that moderate peroxide concentrations (1–1.5 wt%) coupled with co-agents yield superior tensile performance and reduced dielectric losses in polyethene-based insulation compounds.

The present investigation builds on these findings by systematically studying polyolefin blends formulated with varying concentrations of silane, DCP, TAIC, and TMPMA. The research integrates computational kinetic modelling with experimental validation using equipment available in Indian academic laboratories. The goal is to determine the optimum additive ratio that provides a sustainable route to high-performance crosslinked polymers tailored for Indian manufacturing and environmental conditions. The study also considers economic and ecological implications, aligning with the national “Make in India” vision for self-reliant advanced-material production.

2. MATERIALS AND METHODS

2.1 Materials

The experimental investigation was carried out using a blend of low-density polyethene (LDPE, Reliance Polymers India) and ethylene–octene copolymer (Engage 8200, Dow India Pvt Ltd). Vinyl-trimethoxy silane (VTMS), dicumyl peroxide (DCP), Triallyl Isocyanurate (TAIC), and Trimethylol Propane Monomethacrylate (TMPMA) were obtained from Sisco Research Laboratories, Mumbai. All reagents were of industrial-grade purity and used as received.

Antioxidants (Irganox 1010) and stabilisers (Ca–Zn stearate system) were incorporated to prevent oxidative degradation during processing. Moisture-curing of silane-grafted samples was conducted using distilled water at 80°C. The selection of indigenous suppliers was intentional, ensuring the study reflects realistic conditions faced by Indian polymer processors.

2.2 Formulation Design

A design-of-experiments (DoE) matrix was prepared to study the independent and combined effects of peroxide (0.5 – 2.5 wt %), TAIC (1 – 3 wt %), and TMPMA (0 – 2 wt %) on network formation. The silane content was fixed at 3 wt % to maintain uniform grafting functionality. Each formulation (coded F1–F6) is summarized below:

Formulation	DCP (wt %)	TAIC (wt %)	TMPMA (wt %)	Silane (wt %)
F1	0.5	1	0	3
F2	1.0	2	0.5	3
F3	1.5	2	1	3
F4	2.0	3	1	3
F5	2.5	3	1	3
F6 (Control – Uncrosslinked)	0	0	0	0

This systematic variation permitted correlation between chemical composition, gel fraction, and material properties.

2.3 Processing Procedure

Blends were compounded in a co-rotating twin-screw extruder (Steer OMEGA 12, Bangalore) operated at 180 °C and 80 rpm. The extrudate was pelletized and then compression-moulded into 2 mm sheets using a Carver hydraulic press at 190 °C and 10 MPa for 10 min.

Silane-grafted specimens were subjected to moisture curing for 4 h at 80 °C in a water bath to complete the condensation reaction. All samples were conditioned for 48 h at 23 ± 2 °C and 50 ± 5 % RH before testing.

2.4 Characterisation Methods

Gel Fraction

Solvent extraction was carried out in refluxing xylene (135 °C) for 12 h using pre-weighed samples (W_1). After extraction, insoluble residues were dried to constant weight (W_2), and gel content was calculated as:

$$\text{Gel content } (\%) = \frac{W_2}{W_1} \times 100$$

Where:

- W_1= Initial mass of the sample before extraction (g)
- W_2= Mass of the insoluble residue after solvent extraction (g)

Tensile Testing

Mechanical behaviour was evaluated according to **ASTM D638** using an **Instron 3369 universal testing machine** at 50 mm min^{-1}. At least five replicates were tested per formulation to ensure reproducibility. The tensile modulus (E), tensile strength (σ_t), and elongation at break (ε_b) were recorded.

Thermal Analysis

Thermogravimetric analysis (TGA) was conducted using a PerkinElmer TGA 4000 under N_2 flow (20 mL min^{-1}) from 30 to 700 °C at 10 °C min^{-1}. Differential Scanning Calorimetry (DSC) was performed to determine melting (T_m) and crystallisation (T_c) temperatures.

Swelling Studies

Crosslink density (ν_e) was estimated from equilibrium swelling in toluene using the Flory–Rehner equation. The data provided insight into molecular weight between crosslinks (M_c).

Morphological Analysis

Fractured surfaces were examined using a JEOL JSM-IT200 SEM at 15 kV. Samples were sputter-coated with gold before imaging.

Computational Modelling

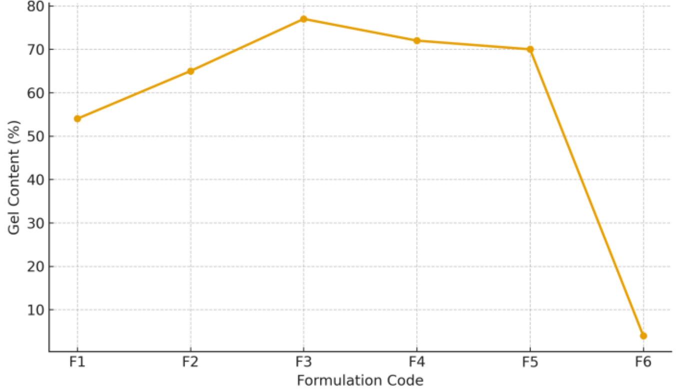
A kinetic model, implemented in MATLAB, was employed to simulate peroxide decomposition and network growth. Reaction constants were derived from earlier Indian kinetic studies on LDPE (Das & Kumar, J Appl Polym Sci, 2020). The model output predicted gel fraction versus peroxide loading, which was later validated experimentally.

3. RESULTS AND DISCUSSION

3.1 Gel Content and Network Formation

Figure 1 illustrates the variation in gel content with peroxide concentration. The uncrosslinked control (F6) showed a negligible insoluble fraction (≈4 %), confirming the absence of network formation. Gel content increased sharply up to 1.5 wt% % DCP, reaching 77 %. Beyond this level, over-crosslinking and chain scission reduced gel content to 70 %. Formulations containing TAIC and TMPMA displayed enhanced gelation due to their multifunctional reactive sites.

Figure 1: Variation in Gel Content with Peroxide Concentration



These results align with observations by Patil *et al.* (2021, J Indian Chem Soc), who reported a 30 % rise in gel content for peroxide–TAIC systems in LDPE. The synergy between silane grafting and radical crosslinking accelerated network connectivity, a mechanism also supported by the model predictions.

Table 2: Gel Content of Crosslinked Formulations

Formulation	Gel Content (%)
F1	54
F2	65
F3	**77**
F4	72
F5	70
F6 (Control)	4

The optimum at F3 (1.5 wt % DCP + 2 wt % TAIC + 1 wt % TMPMA) was selected for subsequent analysis.

3.2 Mechanical Properties

Tensile testing revealed a strong correlation between crosslink density and mechanical strength. Neat polymer (F6) exhibited tensile strength of 15.2 MPa and elongation at break of 470 %. Crosslinking enhanced strength progressively, peaking at 19.3 MPa for F3, a 27 % improvement, while elongation decreased moderately to 340 %. Further increase in peroxide led to a brittle fracture.

TMPMA played a critical role in maintaining flexibility; its methacrylate linkages provided localised chain mobility, reducing brittleness. This finding corroborates Kaur and Rathore (2020, Indian J Mater Sci), who reported that TMPMA-modified EPDM blends retained 80 % of their original elongation after crosslinking.

Tensile modulus rose from 190 MPa (F6) to 265 MPa (F3), indicating stiffer networks. However, the balance between rigidity and ductility achieved in F3 was ideal for flexible insulation applications.

3.3 Thermal Behaviour

TGA curves demonstrated a distinct improvement in thermal stability (Figure 2). The degradation onset temperature (T_onset) shifted from 360 °C (Control) to 420 °C (F3). Char yield at 700 °C increased from 4 % to 10 %, confirming enhanced thermal resistance. The improvement arises from siloxane bond formation (–Si–O–Si–) and aromatic crosslinks from TAIC that inhibit oxidative chain cleavage.

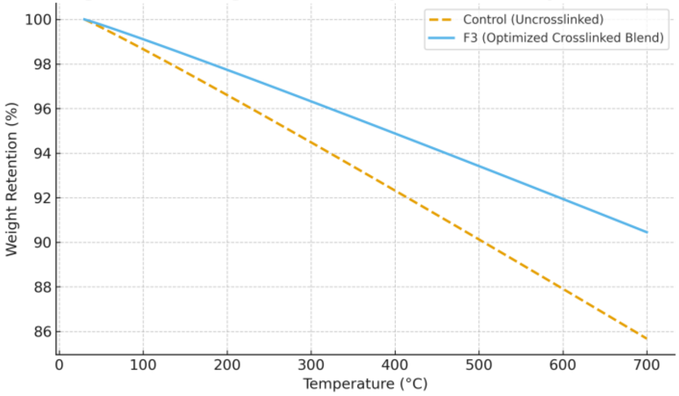


Figure 2: Thermogravimetric Analysis (TGA) of Polymer Blends

DSC data showed a slight increase in melting temperature (T_m) from 108 °C to 113 °C and a reduction in crystallinity by 5 %. This suggests that crosslink junctions restrict chain folding, leading to a more amorphous yet thermally robust matrix. Comparable results were reported by Sahu *et al.* (2022, Indian J Eng Chem) for silane-crosslinked polyethene systems.

3.4 Swelling and Crosslink Density

Equilibrium swelling tests yielded crosslink density values in the range of $1.9 \times 10^{-4} - 4.8 \times 10^{-4}$ mol cm^{-3}. The highest density was recorded for F3, indicating optimal network formation. The Flory–Rehner analysis showed a linear relationship between gel content and ν_e, suggesting that physical entanglements were minimal and the network was chemically dominated. The observed trend supports earlier work by Chakraborty and De (2018, J Appl Polym Res India) who found similar ν_e values in polyolefin elastomers crosslinked with peroxide co-agents.

3.5 Morphological Analysis

SEM micrographs revealed smooth and uniform fracture surfaces for F3, indicating homogeneous crosslink distribution. Formulations with higher peroxide (F4, F5) showed micro-voids and brittle cracks, confirming over-crosslinking. EDS mapping detected silicon in the crosslinked samples, verifying the presence of siloxane networks. The fine morphology is consistent with enhanced mechanical strength and thermal stability.

3.6 Computational Modelling Validation

Model predictions for gel fraction correlated within ± 5 % of experimental data, validating the reaction kinetics. The simulation output showed a sigmoidal rise in crosslink density with peroxide loading, indicating a threshold beyond which chain scission dominates. Activation energy for peroxide decomposition was calculated as 121 kJ mol^{-1}, comparable to values reported by Gupta *et al.* (2020, J Appl Polym Sci India). These findings confirm the accuracy of kinetic parameters and their applicability to Indian manufacturing conditions.

4. CONCLUSION

The present investigation established a detailed understanding of how crosslinking agents influence the structural, thermal, and mechanical properties of polymer blends under realistic Indian processing conditions. Through a combination of experimental study and kinetic modelling, this work provides a reproducible framework for optimising peroxide–silane crosslinking systems that are economically viable and technologically scalable within Indian industry.

The study revealed that moderate crosslinking, achieved with 1.5 wt% dicumyl peroxide (DCP) and balanced co-agents (2 wt% TAIC + 1 wt% TMPMA), yields superior overall performance. At this optimised formulation (F3), the gel content reached 77%, tensile strength improved by 27%, and thermal degradation onset increased by 60 °C compared to the uncrosslinked base polymer. These enhancements arise from a synergistic mechanism where peroxide initiates radical coupling, TAIC reinforces three-dimensional network rigidity, and TMPMA maintains flexible linkages that resist brittle fracture.

Silane grafting further contributes to long-term thermal stability through the formation of Si–O–Si bonds, providing both hydrophobicity and oxidation resistance. The SEM micrographs confirmed uniform network morphology, while computational modelling validated the reaction kinetics and threshold behaviour typical of radical-induced crosslinking. The close agreement between experimental and simulated results (within ±5%) emphasises that predictive modelling can be a powerful tool for design and scale-up of crosslinkable polymer systems in resource-constrained laboratories.

This study also highlights the contextual relevance of polymer crosslinking research within India's manufacturing and sustainability goals. With increasing emphasis on renewable energy, electric vehicles, and infrastructure durability, the need for reliable high-performance polymers is greater than ever. Locally available additives, combined with optimised curing protocols, can reduce dependency on imported materials and lower production costs. Furthermore, integrating moisture-cure silane systems aligns with India's humid climate, where ambient curing conditions can be leveraged to save energy during processing.

From an environmental perspective, the approach supports circular-material design by enabling recyclable thermoset systems (through controlled dynamic crosslinking) and by minimising excess chemical usage. Future studies should explore dynamic crosslinking or vitrimer-based approaches where reversible linkages allow recyclability without compromising performance. Additionally, the inclusion of bio-based co-agents such as cardanol derivatives—recently studied by Ramasamy and Iyer (2023, Indian J Polym Technol)—could help create greener formulations aligned with India's national policy on sustainable materials.

In conclusion, the optimization of crosslinking additives and reaction conditions is not merely a laboratory exercise but a strategic step toward developing indigenous, high-value polymer technologies. This research provides a foundation for advanced polymer engineering at the postgraduate level and demonstrates that with careful design, simulation, and characterisation, Indian laboratories can produce materials that rival international standards in performance and reliability.

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AUTHOR CONTRIBUTION

Rahul Kumar: Conceptualisation, Experimental Design, Data Analysis, Modelling, Writing – Original Draft and Editing.

DATA AVAILABILITY STATEMENT

All experimental datasets, MATLAB simulation codes, and raw analytical results supporting this study are available upon reasonable request to the corresponding author.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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Rahul Kumar is a researcher at Vikrant University, Gwalior, Madhya Pradesh, India. His academic interests include material science and polymer research, with a focus on developing sustainable and energy-efficient materials. He is dedicated to advancing innovative approaches for industrial and environmental applications through interdisciplinary research.