Investigating crosslinking density in the curing process of UV-cured nanocomposites using dynamic mechanical thermal analysis

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Abstract
This study investigates the crosslinking density of UV-cured nanocomposites using Dynamic Mechanical Thermal Analysis (DMTA). Urethane acrylate resins were modified with varying percentages of polyaniline (PANI) (1%, 3%, and 5%) to evaluate the impact on crosslinking behavior and mechanical properties. DMTA was employed to measure key parameters such as storage modulus (E'), loss modulus (E"), and tan δ, which were correlated with crosslink density. Results indicate that the addition of PANI influences the crosslinking efficiency, with optimal performance observed at 3% PANI, where crosslink density (ν) reached 53.182 mol/m³. At higher PANI concentrations (5%), a decrease in crosslinking efficiency was noted, likely due to phase separation or particle aggregation. The findings demonstrate that PANI content significantly affects the network structure and mechanical properties of the nanocomposites, with implications for optimizing UV-curable resin formulations. This work highlights the utility of DMTA in characterizing crosslinking behavior and provides insights into tailoring material properties for advanced applications.

Keywords: Adhesion, UV cure, Urethane acrylate, Cross-link density, Polyaniline, DMTA

Introduction
UV-curable resins have gained significant attention in recent years due to their rapid curing kinetics, energy efficiency, and versatility in applications ranging from coatings to 3D printing. The performance of these materials is heavily influenced by the degree of crosslinking, which determines key mechanical and thermal properties such as stiffness, toughness, and glass transition temperature (T_g) [1]. Crosslinking is a critical parameter that governs the network structure of the polymer, and its precise measurement is essential for optimizing resin formulations and ensuring consistent product quality. Despite the importance of this parameter, accurately quantifying the degree of crosslinking remains a challenge, particularly in highly crosslinked systems where traditional methods may fall short [2].
Dynamic Mechanical Thermal Analysis (DMTA) has emerged as a powerful technique for characterizing the crosslinking behavior of UV-curable resins. By measuring the viscoelastic properties of a material as a function of temperature or frequency, DMTA provides insights into the molecular mobility and network structure of the polymer [3]. The storage modulus (E'), loss modulus (E"), and tan δ (the ratio of E" to E') are key parameters derived from DMTA that can be correlated with the degree of crosslinking. Recent studies have demonstrated the utility of DMTA in quantifying crosslink density and identifying the effects of curing conditions on network formation [4]. However, the interpretation of DMTA data requires careful consideration of factors such as curing kinetics, sample geometry, and the presence of residual monomers or unreacted functional groups [5].
This paper aims to explore the relationship between the degree of crosslinking in UV-curable resins and their mechanical properties, as measured by DMTA. By reviewing recent advancements in DMTA methodologies and their application to UV-curable systems, this work seeks to provide a comprehensive understanding of how crosslink density influences material performance. Additionally, the challenges associated with measuring crosslinking in complex formulations will be discussed, along with potential solutions to improve accuracy and reproducibility [6]. The findings presented here are expected to contribute to the development of more robust and reliable characterization techniques for UV-curable resins, ultimately enabling the design of materials with tailored properties for specific applications.

Experimental
Materials
Aniline, ammonium persulfate, hydrochloric acid, Isophorone diisocyanate (IPDI), acetylene, triethylamine, hydroxyethyl methacrylate (Merck, Germany), dibutyltin dilaurate and polyethylene glycol 400 (for synthesize of urethane acrylate) and were all purchased from Merck, Germany. Trimethylolpropane triacrylate and benzophenone

was from Sigma-Aldrich (used in formulation for UV curing).

Method

Urethane acrylate, polyaniline, benzophenone and triethylamine were used in the preparation of the composite. To prepare the nano-composite, 10 g of urethane acrylate and polyaniline with different weight percentages of 1%, 3%, 5%, benzophenone was used at a rate of 4% by weight of polyurethane acrylate (0.4 g) and tertiary amine triethylamine was used at a rate of 4% by weight of polyurethane acrylate (0.4 g). The composition was cured by mercury UV irradiation for 1 minute.

Results and Discussion

Tangent delta represents the ratio of loss to storage in a polymer material and its value depends on the network structure and the degree of crosslinking. Increasing the percentage of polyaniline can have different effects on tan δ. At low percentages (1%): tan δ may be higher, indicating greater flexibility and less crosslinking. At medium percentages (3%): an optimization between stiffness and flexibility may occur, and tan δ may decrease, indicating increased crosslinking. At higher percentages (5%): If tan δ increases again, it is likely to indicate phase separation or aggregation of polyaniline particles, affecting the homogeneity of the network. In general, a decrease in tan δ at the glass transition temperature (T_g) indicates increased crosslinking, while an increase may indicate a decrease in structural order and an increase in the rubber phase.

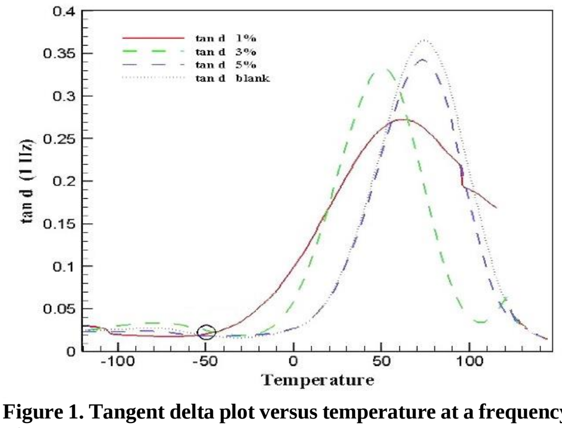

Figure 1. Tangent delta plot versus temperature at a frequency of one hertz.

The crosslinking rate (νe) (νe=E/3RT) decreases with increasing polyaniline (PANI) percentage in urethane acrylate resin. In the pure sample (PU), the value of νe = 39887 mol/m³, but with increasing polyaniline to 1% and 3%, the value increases to 44892 mol/m³ and 53182 mol/m³, respectively, indicating an increase in the crosslinking rate at these percentages. However, in the 5% polyaniline sample, the value of νe = 56994 mol/m³ reaches its lowest value. This decrease indicates a decrease in the crosslinking efficiency at higher polyaniline concentrations, which could be due to the formation of heterogeneous regions and particle aggregation. Therefore, the optimum crosslinking rate is observed at 3% polyaniline, while at 5% it may indicate dispersion limitations or phase separation.

Table 1- Changes in crosslinking density in nanocomposites at a frequency of one Hz.

Nanocomposite	T_g (C°)	E´(MPa)	ν_e(mol/m^3)
PU-0%PANI	74.62	115.27	39887.39
PU-1%PANI	61.68	124.91	44892.35
PU-3%PANI	44.89	142.76	53182.31
PU-5%PANI	73.19	164.03	56994.13

Conclusion

The study demonstrates that the incorporation of polyaniline into urethane acrylate resins significantly influences crosslinking density and mechanical properties. Optimal crosslinking was achieved at 3% PANI, while higher concentrations led to reduced efficiency due to potential phase separation. DMTA proved to be an effective tool for analyzing the network structure and crosslinking behavior of UV-cured nanocomposites. These findings offer valuable insights for optimizing resin formulations to achieve desired mechanical properties, paving the way for enhanced performance in applications such as coatings and 3D printing.

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