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Synthesis, Mechanical Properties and Thermal Stability of Polydimethylsiloxane Nanocomposites

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Abstract

The polydimethylsiloxane/nano-graphite (PDMS-NG) nanocomposites were prepared via a two rolled mixing mill and subjected to characterization using techniques such as Transmission Electron Microscopy (TEM), stress-strain analysis during elongation, as well as thermal properties including Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The transition temperature was observed to be below -70°C for PDMS nanocomposites reinforced with Nano-Graphite (NG). The thermogram from the thermo-gravimetric analysis indicated that at 10%, 20%, 30%, and 50% weight loss, the temperatures for PDMS nanocomposites were higher compared to unfilled PDMS. These findings suggest a substantial improvement in the thermal stability of PDMS-NG nanocomposites.

Keywords: *Mechanical Properties, Nanocomposites, Nano-graphite, Polydimethylsiloxane, Thermal Properties*

1.0 Introduction

To enhance the performance of polymers for practical applications, the incorporation of inorganic fillers has been a common practice. Traditional fillers like carbon blacks, silica, talc, and clays, have traditionally been used for this purpose. However, newer fillers such as nano-graphite, nano-clay, carbon nanotubes, and carbon silica dual phase filler have emerged as challengers to the dominance of these conventional fillers. One advantage of utilizing nano scale fillers is their significantly high surface to volume ratio, which promotes stronger interactions between filler and the polymer, resulting in improved properties.

Over the past few years, extensive research has focused on nano-particle based composites, particularly the reinforcement of plastics[1-3] and polymers with nano-clay[4,5]. Additionally, graphite offers additional benefits such as excellent thermal and electrical conductivity, along with a favorable affinity for polymers[6-8] and organic compounds. This affinity allows for the absorption of certain monomers and polymers into the pores and galleries of graphite[9-11]. While the addition of nano-graphite in polymer matrices has been extensively studied, its effects on PDMS matrices have not been reported.

The objective of this study is to investigate the mechanical characteristics, and thermal studies of nanocomposites comprising PDMS (Polydimethylsiloxane) reinforced with nano-graphite. We examined how varying concentrations of nano-graphite impact the results obtained from both the thermo-gravimetric analysis and differential scanning calorimetry of the PDMS nanocomposites. The composition of the prepared nanocomposites was determined using TGA, while the specific components were identified through Derivative Thermo-Gravimetry (DTG). Additionally, we determined the glass transition temperature (T_g) using DSC.

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2.0 Materials and Methods

2.1 Materials

Polydimethylsiloxane was obtained from Sigma-Aldrich India Pvt. Ltd., Bangalore. Nano Graphite (NG) with a purity of at least 95% was acquired from NANOCYL, Belgium. Prior to utilization, the NG underwent treatment with an acid mixture under ultrasonication to eliminate metallic impurities and amorphous carbon. Chemically pure grade Zinc Oxide (ZnO), Di-Cumyl Peroxide (DCP) and stearic acid, sourced from reputable suppliers, were employed as curing agents.

2.2 Sample Preparation

The polymer was produced by compounding the components following the specified formulation outlined in Table 1. The compounding procedure started with the use of a brabender plastograph, operating at a speed of 60rpm, followed by two roll mixing mill (sized 325x150 mm) with a friction ratio of 1:1.25, adhering to the guidelines of ASTM D 3182 standards. Special attention was given to regulating temperature, nip gap, mixing duration, and ensuring a consistent cutting process throughout the compounding. The mixing temperature was kept in the range of 65–70°C. After completing the compounding process, the polymer compositions were shaped using an electrically heated Moore hydraulic press. The molding was performed under a pressure of 10MPa and at a temperature of 160°C, following molding conditions specified by the Monsanto Rheometer (R-100) as per ASTM D2084 and ASTM D5289 protocols.

2.3 Testing

2.3.1 Mechanical Studies

The tensile strength and modulus of dumbbell-shaped specimens were evaluated using a Hounsfield H10KS Universal Testing Machine following the ASTM D 412 procedure. Five specimens per sample were tested for each property, and the average values are reported based on these measurements.

2.3.2 Thermo-Gravimetric Analysis (TGA)

Thermogravimetric study was performed on PDMS-NG nanocomposites utilizing a NETZSCH STA 409PC/PG instrument in both high-resolution modes and conventional (heating rate). The analysis was conducted over a temperature range from room temperature to 1000°C, employing a heating rate of 10°C/min. All analyses were performed using a 20mg sample. The conventional TG analysis was conducted within a nitrogen atmosphere. The temperature at which the maximum mass loss rate (T_{max}) occurred was determined from the curves obtained in Differential Thermo-Gravimetry (DTG).

2.3.3 Differential Scanning Calorimetry (DSC)

DSC was used to measure the properties of PDMS-NG nanocomposites. The DSC experiments were conducted using a Q-2910 differential scanning calorimeter by TA Instruments, USA. The heating rate employed was 10°C/min, and an aluminum pan was utilized as the standard cell. Measurements were conducted within a temperature range from -150°C to 100°C.

Table 1. Formulations of PDMS and PDMS/NG nanocomposites

Ingredients	**PDMS/NG1 (gms)**	**PDMS/NG2 (gms)**	**PDMS/NG3 (gms)**	**PDMS/NG4 (gms)**	**PDMS/NG5 (gms)**
PDMS	100	100	100	100	100
Nano-Graphite (%)	0	2	4	6	8
Every mix consists of Stearic Acid 2 %, ZnO 5 % and DCP 2 %.					

2.3.4 Scanning Electron Microscopy (SEM)

The SEM was utilized to image the morphology of the PDMS-NG nanocomposites. The prepared samples were securely attached to sample studs using double-sided adhesive tapes. Before conducting the SEM measurements, a thin layer of gold was deposited onto the sample surface through a sputtering process. To determine the average size of the dispersed NG, photomicrographs were captured and analyzed using the Roentec Scan Vision software, developed by Hitachi Corp. in Japan.

2.3.5 High Resolution Transmission Electron Microscopy (HR-TEM) Studies

The morphology analysis of the PDMS-NG nanocomposites was investigated using HR-TEM. For the HR-TEM investigation, ultra-thin cross sections of the sample were prepared using the Leica Ultra Cut UCT Ultra-cryo microtome instrument, which is equipped with a diamond knife.

3.0 Result and Discussion

3.1 Mechanical Properties

Table 2 presents the mechanical characteristics such as elongation at break, tensile strength, hardness and modulus of PDMS nanocomposites reinforced with nano-graphite. It is evident from the data that as the loading of nano-graphite increases, modulus (at 100%, 200%, and 300%), tensile strength, and hardness values also increase, while elongation at break decreases. At an 8 phr NG loading, PDMS exhibits the highest tensile strength, indicating maximal polymer-filler interaction at this concentration. Nano graphite, distinct from traditional fillers, possesses a highly expansive surface area and a complex, branched structure in its aggregates, leading to strong filler-polymer interaction at the surface. The inclusion of fillers significantly contributes to energy dissipation, elevating the tensile strength of the nanocomposites. When fillers like nano graphite are added, the vacant spaces between the polymer chains are filled, restricting chain straightening and consequently reducing elongation. Furthermore, higher filler loading enhances reinforcement and promotes the formation of additional crosslinks during vulcanization, effectively entrapping the free ends of polymer chains.

Upon incorporating fillers like nano-graphite, the available intermolecular spaces within the polymer chains become occupied, impeding chain straightening and resulting in reduced elongation. The reinforcement effect amplifies with higher nano-graphite content, leading to increased crosslinking during vulcanization, effectively trapping the ends of polymer chains. As the filler loading rises, the matrix experiences progressive reinforcement, initially showcasing a higher elongation at the breaking point. However, as the filler content further increases, the interaction between polymer chains and filler aggregates physically restrains molecular segmental movement, causing a subsequent reduction in elongation at the breaking point.

Hardness demonstrates a continuous rise with increasing crosslinking. The denser networks lead to

Table 2. Mechanical properties of PDMS/NG nanocomposites.

	Hardness (shore A)	Tenile Strength (Mpa)	Elongation at Break (%)	Modulus (100%) Mpa	Modulus (200%) Mpa	Modulus (300%) Mpa
PDMS/NG1	40	5.11	529	1.02	1.76	2.74
PDMS/NG2	42	5.45	506	1.12	1.98	2.92
PDMS/NG3	44	5.76	476	1.24	2.16	3.2
PDMS/NG4	45	6.15	457	1.34	2.28	3.5
PDMS/NG5	47	6.24	442	1.42	2.4	3.7

shorter molecular segments between the crosslinks, resulting in a tighter network and heightened hardness. The considerable hardness value can be attributed to the presence of reinforcing nano-graphite with its significantly extensive surface area within the PDMS matrix.

3.2 Thermo-Gravimetric Analysis

The thermal endurance of the PDMS-NG nanocomposites was evaluated using Thermo-Gravimetric Analysis (TGA) under a nitrogen atmosphere. The TGA plot (depicted in Figure 1) reveals distinct phases. Notably, there is no weight loss up to 300°C, affirming material stability within this temperature span under nitrogen. A primary weight reduction is observed between 300–400°C, attributed to the evaporation of volatile components within the composition. The thermal stability exhibited a notable enhancement with a 6% nano-graphite loading, manifesting in an onset degradation temperature of 369.31°C. Compared to a 2% nano-graphite loading, this marks an approximate 54°C increase in the onset degradation temperature for the PDMS-NG nanocomposites. This improvement is likely attributed to the PDMS intercalating into the nano-graphite structure. Subsequently, another weight reduction transpires within the 450–550°C range, arising from the presence of moderately volatile elastomeric constituents in the composition.[12]

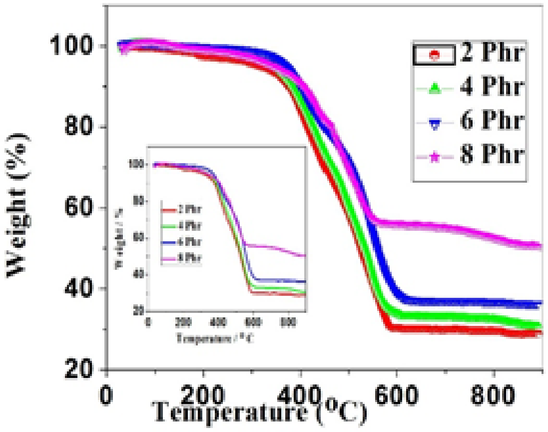

Figure 1. TGA curves for PDMS/NG nanocomposites.

The degradation of PDMS-NG displays a subtle shift towards higher temperature ranges as the nano-graphite loading increases. This shift suggests a robust interaction occurring at the PDMS-nano-graphite interface, resulting in decreased mobility of polymer chains in the vicinity of this interface. The TGA thermogram illustrates that the temperatures corresponding to 10%, 20%, 30%, and 50% weight loss in PDMS-NG nanocomposites increase with greater nano-graphite content. Furthermore, it is observed, as depicted in Table 3, that the 8phr nanocomposites retain a higher residue post-degradation, with a weight loss of approximately 50%. The mass observed at 894°C primarily stems from the residual nano-graphite, aligning with the initial nano-graphite loading.

3.3 Differential Thermo-Gravimetry Analysis

Figure 2 shows the DTG curves for nano-graphite reinforced PDMS nanocomposites. In the DTG curve, the peak temperature (Tp) indicates the temperature at which the highest rate of weight loss is achieved. Tp appears at 407.1 and 528.8°C, 432.4 and 543.1°C, 408.5°C and 549.9°C, 430 and 515.5°C for 2, 4, 6 and 8 phr nano-graphite concentrations. It is significantly increased which show that the addition of nano-graphite significantly

Table 3. TGA data for PDMS/NG nanocomposites.

	T_5 at °C	T_{10} at °C	T_{20} at °C	T_{30} at °C	T_{50} at °C	**Residue at 894°C wt%)**
PDMS/NG1	323.06	380.06	414.06	450.06	525.06	33.5 %
PDMS/NG2	345.22	385.23	427.23	468.23	533.23	34.02 %
PDMS/NG3	369.31	399.31	448.31	503.31	558.31	36.35 %
PDMS/NG4	340.85	404.85	462.85	496.85	848.0	50.40 %

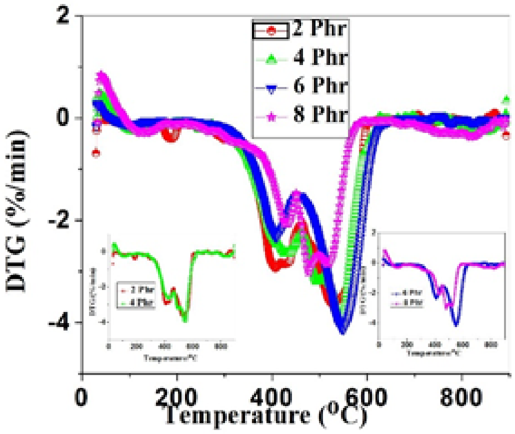

Figure 2. DTG curves for PDMS/NG nanocomposites.

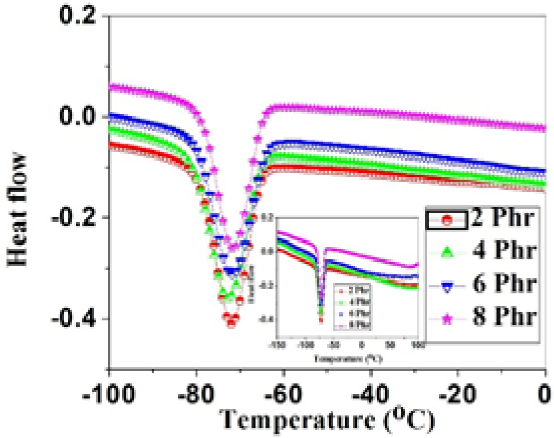

Figure 3. DSC curves for PDMS/NG nanocomposites.

improved the thermal stability of PDMS in nitrogen atmosphere.

3.4 Differential Scanning Calorimetry

To analyze how varying nano-graphite loadings impact the material properties, DSC analysis was conducted on PDMS-NG nanocomposites. Figure 3 illustrates the DSC curves obtained from this analysis.

The DSC curves provided a basis for analyzing the thermal properties of the specimens. It's notable that a transition temperature (T_β) is observed below -70°C. The interactions involving adsorption at the polymer-filler interface significantly influence the thermal properties of the composite systems, particularly the crystallization process. In addition to the low glass transition temperature, DSC measurements reveal a crucial characteristic of PDMS-NG— an exothermic peak associated with crystallization. As depicted in the figure, it is evident that both the degree of crystallinity (calculated from the peak area) and the crystallization temperature decrease with an increase in nano-graphite loadings, as outlined in Table 4.

3.5 Morphology

Attaining a uniform distribution of nano-graphite throughout a polymer matrix holds significant importance, as any irregularities can lead to structural flaws in composite materials. Hence, it is imperative to comprehensively assess the morphological features to investigate the dispersion of NG within the polymer matrix. Figure 4(a-d) showcases photomicrographs of PDMS nanocomposites with differing weight percentages of nano-graphite, offering valuable insights into their dispersion characteristics.

The figure clearly demonstrates that the nano-graphite particles within the PDMS matrix exhibit a random orientation, forming an interconnected network. In Figure 4a, individual dispersion of nanographites is observed within the PDMS matrix. Furthermore, even in PDMS-NG nanocomposites with 6wt% (Figure 4c) and

Table 4. Thermal property parameters of PDMS/NG nanocomposites

	T_g °C	**Degree of crystallinity (Area under the peak)**
PDMS/NG1	-72°C	-17.06 J/g
PDMS/NG2	-72.8 °C	-17.53 J/g
PDMS/NG3	-71.9 °C	-16.14 J/g
PDMS/NG4	-71.7 °C	-15.19 J/g

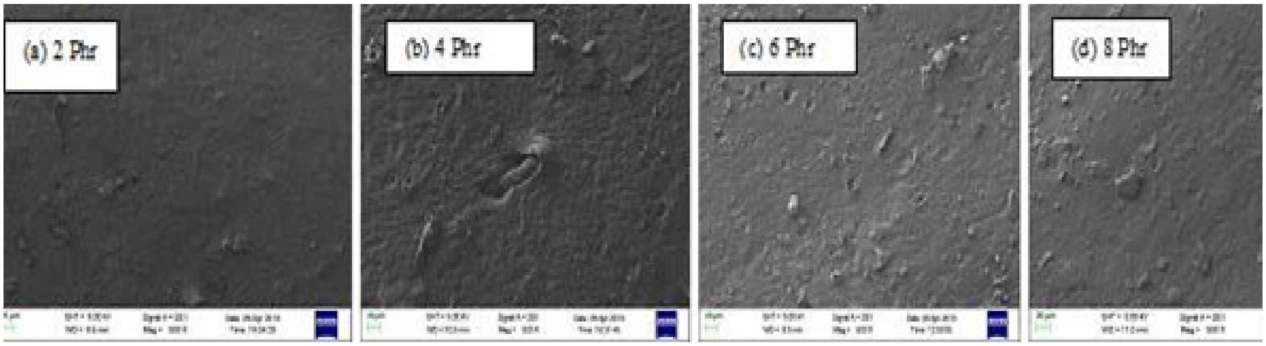

Figure 4. SEM photomicrographs of PDMS/NG nanocomposites: Effect of nano-graphite loadings.

8wt% (Figure 4d) nano-graphite loading, a well-dispersed pattern is evident, although small agglomerates become more apparent as the nano-graphite weight percentage increases in the PDMS matrix. This observation is consistent with the SEM photomicrograph, and it aligns with the mechanical property results. The SEM micrographs presented in Figure 4 (a-d) depict an excellent distribution of nano-particles throughout the PDMS matrix. Additionally, an increase in filler concentration corresponds to an enhanced density of the conductive network, as observed.

3.6 Fracture Surface Morphology

For visualizing the arrangement and integration of nano-graphite as well as their physical interaction with the PDMS matrix, fractured surface morphology of PDMS-NG nanocomposites are presented in Figure 5. The luminous dots and filamentous structures evident in the images can be attributed to nano-graphite within the PDMS matrix. The figure distinctly illustrates an increased presence of these bright dots and thread-like structures in composites with higher NG loading. Through SEM images at lower magnifications, it is evident that at lower loadings of NG (2 and 4 wt%), the dispersion is uniform throughout the PDMS matrix. However, higher loading (8 wt%) exhibits notable agglomeration of NGs.

Nonetheless, it is evident that the nano-graphite is evenly distributed within the insulating PDMS matrix. At higher nano-graphite loadings, agglomerates act as foreign bodies and initiate cracks in the nanocomposites under stress, consequently reducing elongation at break. Though the agglomerates are relatively large in size, the sphere-like morphology mitigates their impact as stress concentrators in the composites. Hence, there is no pronounced effect on tensile properties, contributing to an enhanced modulus. However, a substantial quantity of nano-graphite particles dispersed in the elastomer matrix significantly elevates hardness while decreasing the impact strength of the composites.

Micrographs 5 (a) and (b) depicting 2 wt% and 4 wt% loadings respectively reveal a profusion of well-dispersed nano-graphite across the entire surface without

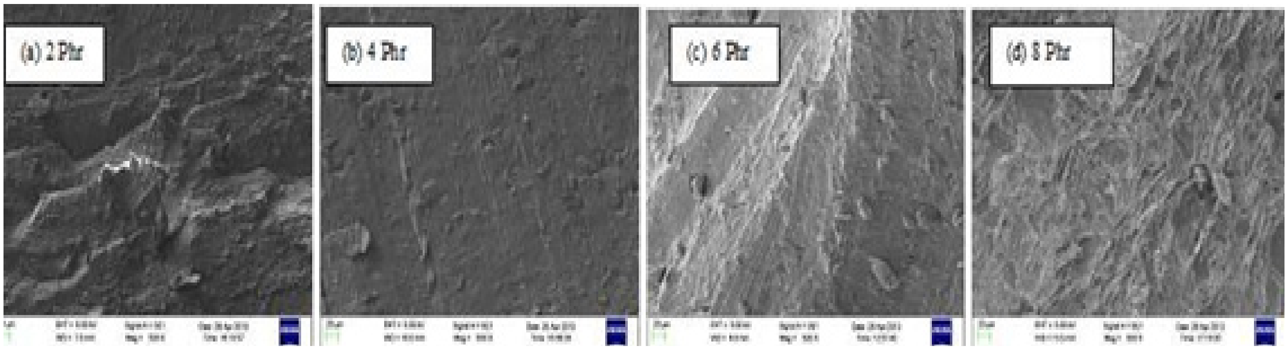

Figure 5. Fractographs of PDMS/NG nanocomposites during tensile deformation .

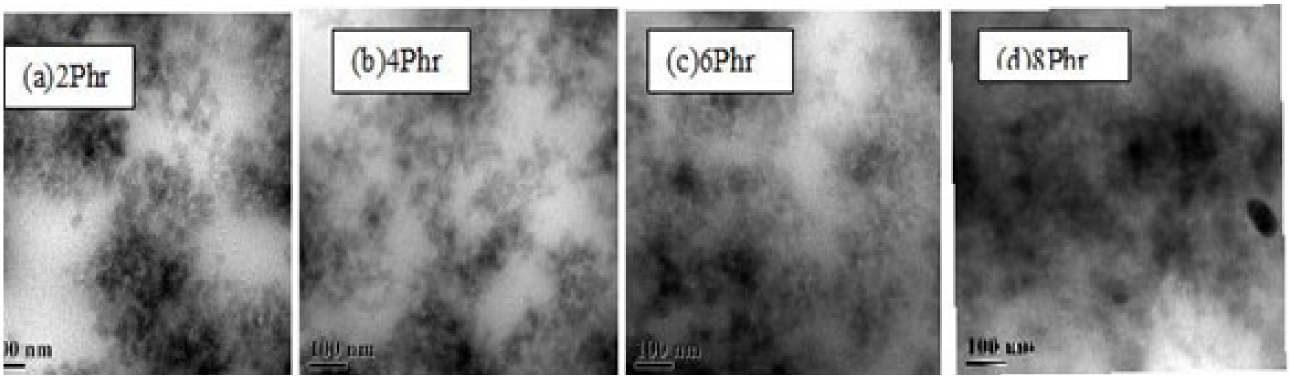

Figure 6. TEM image of PDMS/NG nanocomposites: Effect of NG loadings.

any agglomerations. Conversely, micrographs 5(c) and (d) display agglomerations of NG, likely due to self-aggregation facilitated by Vander Waals bonding and insufficient interfacial adhesion between NG and the PDMS matrix. Another plausible explanation could be that the filler-filler interaction surpasses the polymer-filler interactions.

3.7 HR-TEM Analysis

The HR-TEM analysis (Figure 6) provided further insights into the distribution of NG particles within the PDMS matrix. The dark spots observed in the images were identified as nano-graphite and displayed excellent exfoliation within the PDMS matrix. Exfoliation, in this context, refers to the degree to which nano-graphite particles are effectively deaggregated. Some regions showed minor degrees of aggregation in the NG, which is expected as these NG particles were unmodified. Additionally, the images demonstrated remarkable alignment along the fiber axis. The alignment of polymer chains alongside nano-graphite contributes to the enhanced mechanical properties.

In PDMS nanocomposites reinforced with 6 and 8 Phr of NG, larger and more agglomerates were observed, indicating a reduction in PDMS matrix dispersion with an increase in NG loading. The average diameter of the NG, was approximately 25 nm. The wide distance between NGs in the matrix results in favorable orientation with minimal interface interaction between them. These observations highlight the significant role of NG orientation in influencing the stress and strain of the matrix. Another crucial factor impacting mechanical properties is the aspect ratio; a higher aspect ratio leads to increased material strength.

4.0 Conclusions

We have effectively fabricated PDMS nanocomposites with varying NG loadings from 2-8 wt%. Utilizing a mechanical mixing technique, these nanocomposites were synthesized. The SEM micrographs demonstrate a remarkable dissemination of NGs within the polymer matrix, signifying an even dispersion of fillers. However, an increase in NG loading showcases noticeable NG aggregations, notably evident in the SEM photomicrograph of the 8 wt% NG-containing sample. The HRTEM analysis validates the uniform dispersion of NGs throughout the PDMS matrix, although higher loadings (6-8 wt% NG) exhibit some agglomeration. The average NG diameter within the PDMS matrix is approximately 25 nm. As the nano-graphite loading increases, modulus (at 100%, 200%, and 300%), tensile strength, and hardness values escalate, while elongation at the breaking point declines.

The β transition temperature (T_β) manifests below -70°C. TGA thermograms reveal that the temperatures corresponding to 10%, 20%, 30%, and 50% weight loss in PDMS-NG nanocomposites elevate with higher nano-graphite concentrations. Notably, the nanocomposites incorporating 8 wt% NG demonstrate a higher residue post-degradation, accounting for around 50% weight loss. At 894°C, the residual mass is predominantly attributed to the lingering nano-graphite, aligning with the initial nano-graphite loadings. The peak temperature (T_p) on the DTG curve, indicating the point of maximum weight loss rate, notably rises. This underscores the significant enhancement of thermal stability in PDMS due to the inclusion of nano-graphite, particularly under a nitrogen atmosphere.

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