



Preparation of Nanographene-Based Copolymer Nanocomposites: Thermal Decomposition Kinetic, Optical, and Electrical Behaviors

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Abstract

The poly(4-methacryloyloxyphenyl-4'-methoxystyryl ketone-co-methyl methacrylate) [P(MPMESK0.25-co-MMA)] was synthesized using a free radical copolymerization method at 60 °C. The composition of the copolymer was estimated by ¹H-NMR. The nanocomposites of P(MPMESK0.25-co-MMA)-loaded 9 and 11 wt% nanographene (NG) were produced using the ultrasonic homogenizer sonicator. The FT-IR, ¹H-NMR, GPC, TGA, XRD, and SEM techniques were used to characterize the copolymer and composites. The thermal behavior of P(MPMESK0.25-co-MMA) partially heated up to 270, 310, 340, and 380 °C was investigated by FT-IR analysis. A six-membered anhydride ring in the copolymer backbone formed at 340 °C and higher temperatures. TG measurements were used to analyze the thermal decomposition processes of pure P(MPMESK0.25-co-MMA) and P(MPMESK0.25-co-MMA)/NG 11 wt% composite. Apparent activation energies for thermal decomposition of P(MPMESK0.25-co-MMA)/NG 11 wt% were determined using the Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods at a temperature range of 200 and 400 °C for a weight loss of approximately 70%. The average activation energies determined from the FWO and KAS methods were 86.3 and 80.3 kJ/mol, respectively. The dielectric and electrical behaviors of the P(MPMESK0.25-co-MMA) and P(MPMESK0.25-co-MMA)/NG 11 wt% composite were investigated at room temperature. The dc activation energy for dc conductivity of nanocomposite was calculated as 1.092 eV. Optical properties such as absorption, reflectance, refractive index, absorption edge, direct band gap of the copolymer, and composites were investigated from their optical examinations in the wavelength region of 200–800 nm. It was found that the optical energy gap values had shifted to the lower energies with the doping of NG.

Keywords Nanographene · Copolymer · Electrical conductivity · Dielectric properties · Optical properties

1 Introduction

Mixing homopolymers or copolymers with organic and inorganic structures to produce dielectric polymer nanocomposites is a promising way to develop tunable materials. Nanostructures doped into the polymer matrix can attain good permeability and conductivity by achieving a low percolation threshold while maintaining the advantages of polymers. A good dispersion of fillers added to the polymer matrix plays an important role in their molecularly compatible behavior with the polymer matrix. Nanoparticles such

as graphene and graphite can be guided by their compliant behavior within the polymer matrix. This behavior is essential in high-performance capacitor applications [1]. Carbon nanoparticles were doped into polar polymers like polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA), which were used as enhancers in electrochemical detector fabrication [2]. Carbon quantum dots doped into PVA are promising for producing materials that can exhibit membrane behavior [3]. Due to the superior properties of nanographene (NG), such as its high surface area and enormous electron transport capabilities, it has been doped into many guest polymers and enabled the transition from insulating polymer to semiconductor material. Studies on electrical, thermal, mechanical, and gas barrier properties of graphene/polymer nanocomposites have been carried out [4]. The electrical field behavior of a material is determined by its dielectric constant. Polymer composites with a high dielectric constant are suitable for capacitors, insulators, and high-frequency

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electronic components [5]. Polymer composites can also be potentially used in the field of optics. The refractive index is an indicator of the material interaction with light. Polymer composites with a high refractive index can be used in optical fibers and lenses. For this purpose, nanoparticles with a high refractive index can produce polymer composites [6, 7]. Recently, carbon materials such as carbon nanotubes have become much more specialized nanostructured particles. Graphene, graphite, and carbon nanotubes, also called 2D materials, are known to be among the most promising nanofiller materials due to their low density, thermal properties, chemical inert behavior, and good electrical conductivity [8–13]. Some nitrochalcones have been added to PMMA at different concentrations. These materials were reported as potential candidates for photonic and optical limiting applications [14]. In this context, a polymer composite material made by doping a material with strong properties, such as NG, into the copolymer of chalcones made with MMA can also exhibit excellent properties. The nanograph's high surface area relative to its size allows it to have more contact points. This is one of the properties of NG that enables it to be used in various fields of application. Due to this feature, NG has better thermal stability than larger structures and can be used for energy storage, catalysis, and sensors. Its high electrical conductivity makes NG a preferred nanomaterial for electronic device applications, such as transistors, sensors, and memory devices. It has been reported that NG-based transistors exhibit high-speed performance and low power consumption [15–18]. Materials containing NG are also promising for use in supercapacitors and batteries. Previous studies have investigated supercapacitors made of nanographene. As a result of these research initiatives, it was found that these capacitors had high energy and power density, fast charging times, and long cycle lives. Considering the rapid advancement of technology, the production of NG-based materials and research on their properties for various applications, such as electric vehicles and renewable energy storage, are important [19–23].

The synthesis of chalcone group-bearing copolymer and preparation of NG-doped composite materials are essential for optoelectronic, photonic, and energy storage applications. According to a comprehensive literature survey on the copolymer and NG composites synthesized in this study, there is limited information. Therefore, we designed a systematic study on their structural, kinetic, optical, electrical, and dielectric properties. The thermal decomposition kinetics of a nanocomposite was investigated various optical properties of the blends, such as absorption band edge, optical energy band gap, and Urbach energy. Dielectric properties such as dielectric constant (ϵ'), dielectric loss (ϵ'') and loss tangent ($\tan\delta$), and ac/dc electrical conductivity were investigated using an LCR meter. Therefore, in order to better understand how these copolymer, NG-doped materials work

and how they are used in technology, the experimental results are comprehensively described, and several structure–property relationships are discussed.

2 Materials and Methods

2.1 Materials

Methyl methacrylate (Sigma-Aldrich) was purchased. Solvents such as tetrahydrofuran (THF) and 1,4-dioxane were used as received. The NG was received from Nanografi. All of the other reagents were used as provided.

2.2 Preparation

of 4-Methacryloyloxyphenyl-4'-Methoxystyryl Ketone (MPMESK)

4-Methacryloyloxyphenyl-4'-methoxystyryl ketone (monomer) was synthesized according to an adapted method found in the literature [24, 25]. It was prepared from a reaction of 4-hydroxy-phenyl-4'-methoxystyryl ketone with methacryloyl chloride using trimethylamine as a base and tetrahydrofuran as solvent between -5 and 0 °C. The structure of the product was confirmed using the FT-IR and ^1H -NMR techniques.

2.3 Copolymerization of MPMESK and MMA

The copolymerization of MPMESK and MMA was achieved by free radical copolymerization in the presence of 1,4-dioxane as solvent using an AIBN initiator at 60 °C. The product was precipitated within ethyl alcohol. The precipitation process was repeated two times, and the product was dried at 40 °C under a vacuum for 24 h. The synthesis formula of the copolymer is shown in Scheme 1.

2.4 Preparation of Copolymer Nanocomposites

To allow appropriate dispersion of NG in dichloromethane, it was dispersed with an ultrasonic homogenizer sonicator processor for approximately 60 min. The solution in the dichloromethane of the copolymer was later combined with solution in the dichloromethane of NG. The mixture of copolymer and NG was precipitated in ethyl alcohol, and the copolymer nanocomposites were filtered. It was then dried for 24 h under a vacuum at 40 °C.

2.5 Characterization

^1H -NMR analysis was carried out on a Bruker AVANCE-400 NMR instrument. Fourier transform infrared (FT-IR) spectra were recorded at room temperature (range: 4000 – 400 cm^{-1})

Scheme 1 Synthesis of poly(MPMESK) and poly(MPMESK0.25-co-MMA)

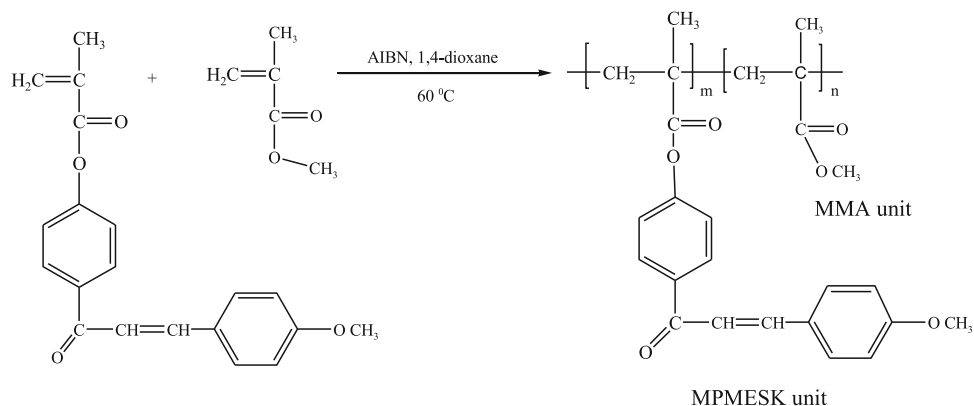
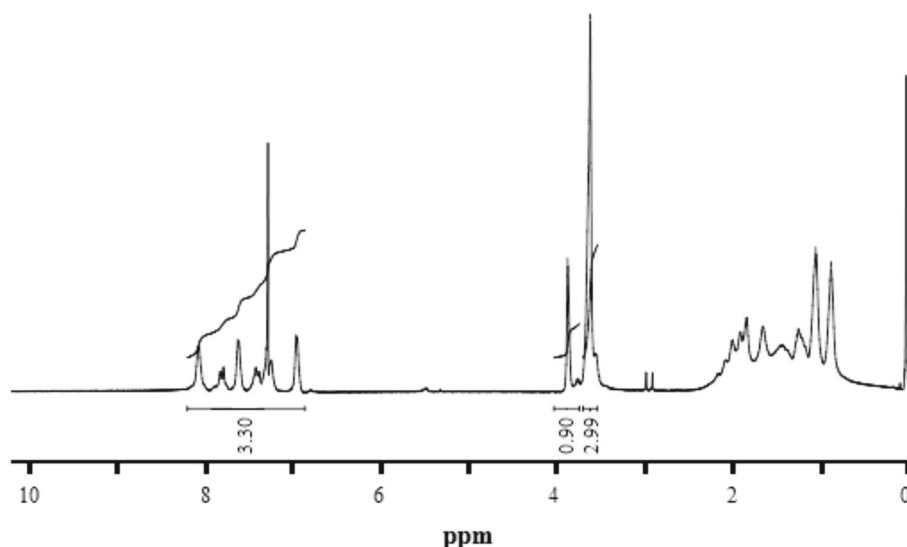


Fig. 1 ^1H -NMR spectrum of P(MPMESK0.25-co-MMA)



using a PerkinElmer Spectrum Two ATR FT-IR spectroscopy. An Agilent 1100 Series Gel Permeation Chromatography (GPC) instrument was used to determine the average molecular weight of the polymer. Thermogravimetric (TGA) measurements were taken using a Shimadzu TGA-50 from room temperature to 500 °C at a heating rate of 10 °C min⁻¹ under argon gas flow (10 mL/min). The X-ray diffraction pattern (XRD, Miniflex 600) was recorded with Bragg's angle (2θ) in the range of 5–80 at a wavelength of 1.5406 (λ). The morphology of the nanocomposite was characterized by scanning electron microscopy (SEM) performed on a field emission scanning microscope (Carl Zeiss EVO MA10). The electrical and dielectric measurements of the pure copolymer and its composites were recorded on tablets prepared under four tons of pressure. The dielectric measurements were taken using an Impedance Analyzer (QuadTech 7600 LRC) between 100 Hz and 10 kHz. The dc electrical conductivities were performed on an FYTRONIX Electric Characterization device. Optical measurements were taken using PerkinElmer Lambda 35 UV spectroscopy.

3 Results and Discussion

3.1 Structure Characterization

The ^1H -NMR spectrum of the MPMESK-MMA copolymer is shown in Fig. 1. As can be seen in the spectrum, CH₃ protons adjacent to ester oxygen at 3.63 ppm for MMA units and CH₃ protons attached to the ether functional group in the chalcone unit are the most characteristic signals. The signal observed at 3.78 ppm originates from the methoxy (OCH₃) group attached to the aromatic ring in the MPMESK units. Signals between 7.25 and 8.08 ppm in the spectrum are due to the aromatic ring protons in the MPMESK's structure. The signal at 6.98 ppm can be attributed to one of the olefinic protons in the cinnamoyl group. The signals of the aromatic protons and the other olefinic protons overlapped, and signals belonging to the methylene protons in the structure of both comonomers are between 2.05 and 1.46 ppm. The signal observed at 1.25 ppm in the spectrum is due to the α-methyl protons in the two comonomer units [25, 26].



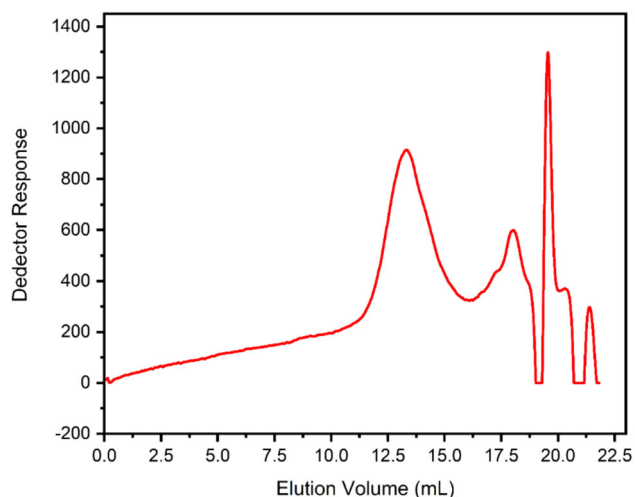


Fig. 2 GPC curve of P(MPMESK0.25-co-MMA)

The copolymer composition was calculated from the integral heights of the aforementioned signals. It was determined that the copolymer composition contains 25% MPMESK by mol. Fourier transform infrared spectroscopy (FT-IR) indicated the important bands at 1751 cm^{-1} ($\text{C}=\text{O}$ in the ester group of MMA), 1660 cm^{-1} ($\text{C}=\text{O}$ stretching in ketone of MPMESK), 1595 cm^{-1} ($\text{C}=\text{C}$ stretching on the two aromatic rings), 1250 cm^{-1} ($-\text{O}-\text{C}$ stretching next to the aryl group), and 1150 cm^{-1} ($\text{C}-\text{O}$ stretching in the ester group) [25, 27, 28].

The gel permeation chromatography (GPC) curve of the polymer was taken with a GPC device calibrated with poly(MMA) in THF solvent (Fig. 2). According to the GPC data, the average molecular weight (M_w) was 81,096 gr/mol, the average molecular weight number (M_n) was 36,831 gr/mol, and the polydispersity index (PDI) was 2.2. Polymer materials with narrow PDI are preferred for industrial applications. Therefore, determining a polymer's PDI value is crucial [29]. The PDI (M_w/M_n) for the copolymer is 2.2, indicating that the chain termination of the copolymer occurred via disproportionation [30].

The thermal behaviors of the copolymer and the 11 wt% NG-doped nanocomposite were investigated using TGA. Previous TGA studies have revealed important information about the nature and degree of the degradation of polymers, composites, and many solid materials. For comparison, the TGA curves of the pure copolymer and nanocomposite are shown in Fig. 3. A detailed evaluation of the TG curves is summarized in Table 1. As shown in Fig. 3, the decomposition onset temperature (T_{onset}) and maximum decomposition temperature (T_{max}) of the copolymer in the nanocomposite and the decomposition temperature (T_{50}) at 50% weight loss shifted to higher temperatures when NG was added to the polymer matrix. Temperature

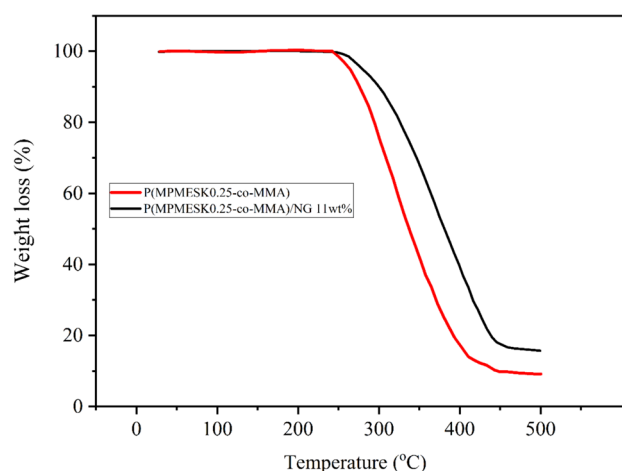


Fig. 3 TG curves for **a** P(MPMESK0.25-co-MMA) and **b** P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposites in nitrogen at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

levels that indicate a 50% weight loss are typically analyzed to evaluate the thermal stability of polymeric materials [31]. P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposite showed a delayed decomposition compared to the neat P(MPMESK0.25-co-MMA). Therefore, the thermal stability of P(MPMESK0.25-co-MMA) was significantly improved in the presence of NG. Why does NG increase the thermal stability of the copolymer nanocomposite? Generally, an increase in the thermal stability of a copolymer nanocomposite is possible because NG is a good material for conducting. Because the thermal conductivity is perfect, it easily takes up and transfers the heat applied to the copolymer nanocomposite. In addition, the segmental mobility of the copolymer chain due to the surface of the NG also increases the thermal stability of the composite compared to the copolymer [32, 33]. In prior studies, the thermal stability of a polymer was found to have significantly improved in the presence of thermally conductive fillers, such as carbon nanotube, NG, and graphite [34–36]. The thermal stability of the copolymer composite prepared in our study is similar to that found in the literature. For example, it was observed that the initial decomposition temperature and the maximum decomposition temperature of P(MPMESK0.25-co-MMA) and NG 11 wt% added composite shifted from 241 to 250 $^{\circ}\text{C}$ and from 335 to 381 $^{\circ}\text{C}$, respectively. This behavior indicates that because NG possessed high thermal stability, it also caused an improvement in the thermal stability of the nanocomposite. In general, when NG is mixed with polymer matrices it knows that a material's thermal stability improvement. In this context, NG particles delay the volatility of the polymer or copolymer by having a barrier effect that hinders the evaporation of volatile products formed at the degradation temperature. This indicates strong interfacial interactions

Table 1 Results of TGA for P(MPMESK0.25-co-MMA) and composite system with NG 11 wt%

Polymer	$T_{\max}^a$	IDT ^b (°C)	Temperatures (°C) at certain wt% weight losses					
			10	30	50	70	90	Residue (%)
P(MPMESK0.25-co-MMA)	335	241	274	308	335	370	442	9.2
P(MPMESK0.25-co-MMA)/NG 11wt%	381	250	300	346	381	417	–	16

^aTemperature for maximum rate of decomposition^bInitial decomposition temperature

between the copolymer matrix and the NG layers [37]. Therefore, NG has a retarding role in the degradation of polymeric materials. It is thermally stable up to 500 °C and does not result in weight loss. Although the weight loss of the pure copolymer was 9.2 wt%, the composite's weight loss was measured as 16%. The results suggest that the NG was thermally stable under argon gas flow and did not result in weight loss up to 500 °C. This behavior indicates that NG remained intact in the polymer matrix.

3.2 SEM and EDX Analysis of Nanocomposite

Figure 4a and b shows the SEM micrographs of the P(MPMESK0.25-co-MMA) and P(MPMESK0.25-co-MMA)/NG 11 wt% composite. The SEM micrographs also confirm the 2D shape of the NG and the stacking together of graphene sheets in the copolymer system. Many of the special properties of graphene have been attributed to its extremely thin structure. Its optical transparency has also been attributed to this thinness [38, 39]. It has been reported that the surface of graphene nanosheets is smooth, transparent, and wrinkled [40]. As indicated in Fig. 4a, the image of P(MPMESK0.25-co-MMA) has a high surface porosity. The stacking together of NG sheets is an important reason for the decreased flexibility of NG the copolymer matrix to a greater extent; this explains the influence of NG on copolymer properties. Compared to the copolymer matrix, the morphology of the copolymer/NG composite is rough and ridged. In a copolymer nanocomposite-loaded NG 11 wt%, there is a uniform distribution of NG in the copolymer matrix, as shown in Fig. 4b. In addition, as indicated in Fig. 4c, EDX analysis shows that the carbon percentage from the sections taken in the SEM image is around 95%. These data show the presence and homogeneous distribution of NG particles in the copolymer matrix. The distribution of NG sheets in the copolymer matrix significantly influences the thermal decomposition behavior of the P(MPMESK0.25-co-MMA)/NG composite.

3.3 XRD Analysis

XRD patterns recorded from the P(MPMESK0.25-co-MMA)/NG 11 wt% powder nanocomposites are shown in

Fig. 5. The XRD pattern of polymer nanocomposite powder shows a sharp and strong diffraction peak at a 2θ of 26.5° which corresponds to the interlayer d-spacing ($d = 3.36\text{\AA}$) in NG [41, 42]. The strong peak at diffraction angle 2θ of 26.5° is the interlayer d-spacing of the graphene plates. A broad amorphous peak from P(MPMESK0.25-co-MMA) was observed around 14.83° , corresponding to a d-spacing of $5.96\text{\AA}$. This confirms that P(MPMESK0.25-co-MMA) has an amorphous microstructure. When the NG filler was 11 wt%, the intensity of the diffraction peak was stronger, confirming the increased amount of NG in the copolymer composite at high NG loading. No peak shift was observed in the XRD pattern.

3.4 FT-IR Relationship—Residue During Partial Degradation of Copolymer System

FT-IR is an effective analytical technique for functional group analysis used to study changes in functional groups in polymers against external influences. In this context, polymeric materials have bonds and functional group properties that identify them. Therefore, the TGA and FT-IR techniques were used to reveal the thermal behavior of the copolymer system. As shown in Fig. 3, the weight losses at 270, 310, 340, and 380 °C under argon gas flow at a heating rate of 10 °C/min were 6, 31, 51, and 76%, respectively. As shown in Fig. 6a–e, the FT-IR spectra of the copolymer residues remaining at these weight losses were recorded for the above-mentioned temperatures, and those that occurred after each heating step are compared in the figures. Figure 6a indicates the FT-IR spectrum of unheated P(MPMESK0.25-co-MMA), where the following bands were identified: $2948\text{--}2838\text{ cm}^{-1}$ (C–H stretching methylene and methyl groups), 1728 cm^{-1} (C = O stretching of the ester group in both units), and 1660 cm^{-1} (keton C = O stretching in the chalcon group). When the FT-IR spectra of the copolymer partially heated to 270 °C (Fig. 6b) and 310 °C (Fig. 6c) were compared to the unheated copolymer (Fig. 6a), the FT-IR spectra were almost similar to each other. However, especially when the temperature increased to 340 °C (Fig. 6d), significant changes were observed in the bands of some functional groups in the



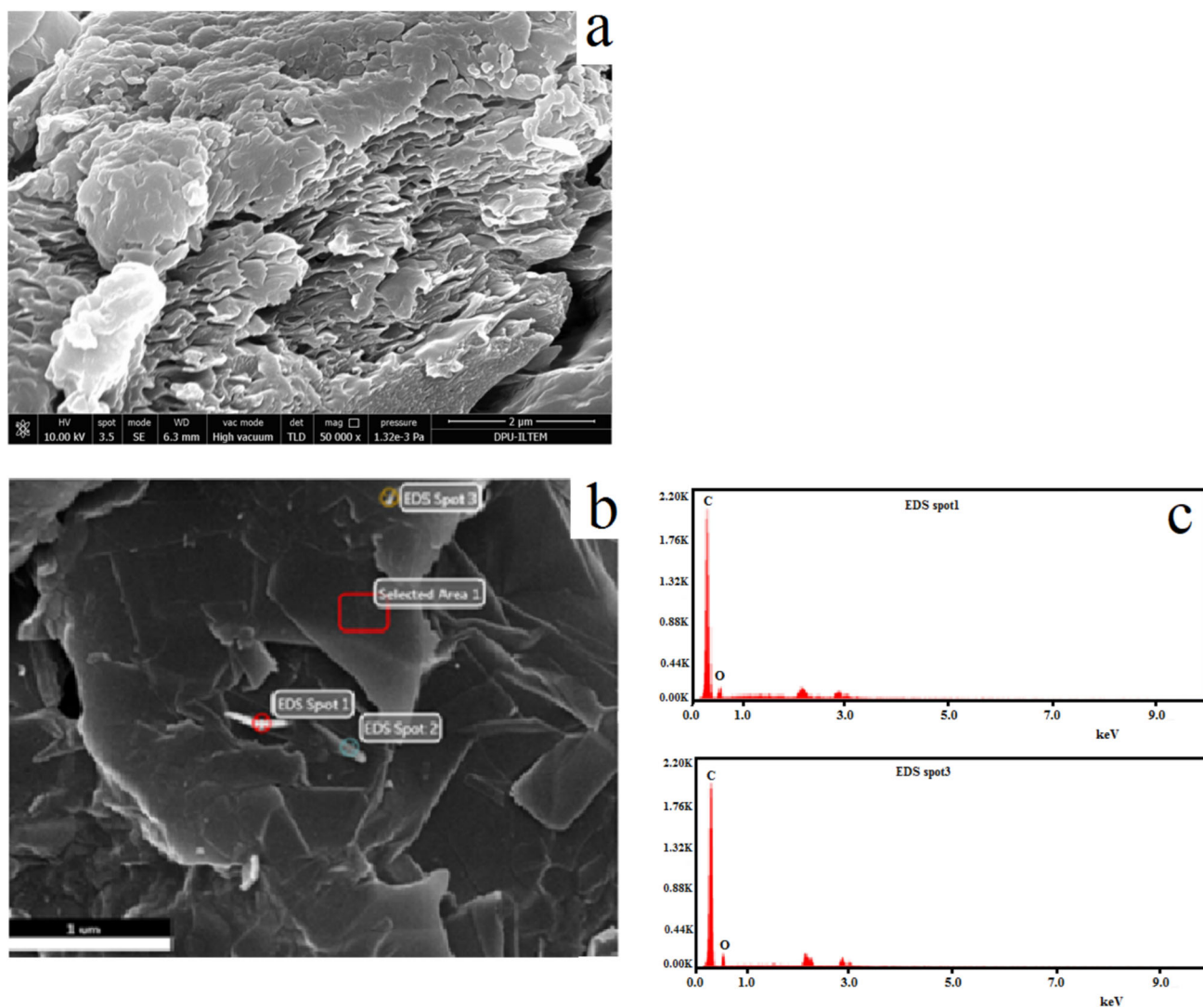
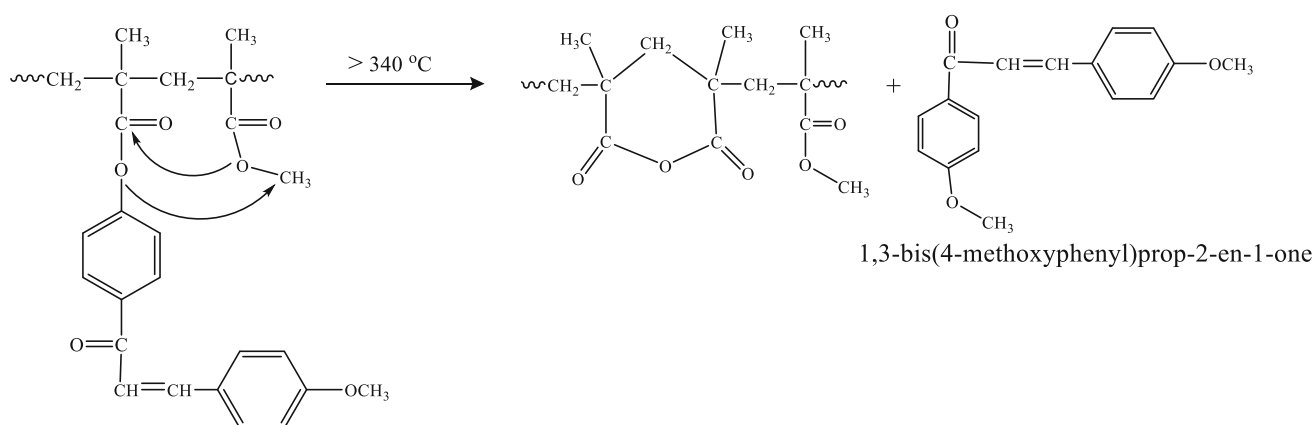


Fig. 4 a SEM image of P(MPMESK0.25-co-MMA), b SEM image of P(MPMESK0.25-co-MMA)/NG 11 wt%, and c EDX analysis of P(MPMESK0.25-co-MMA)/NG 11 wt%



Scheme 2 Proposed degradation pathway for forming a six-membered anhydride ring via degradation of the copolymer system above 340 °C

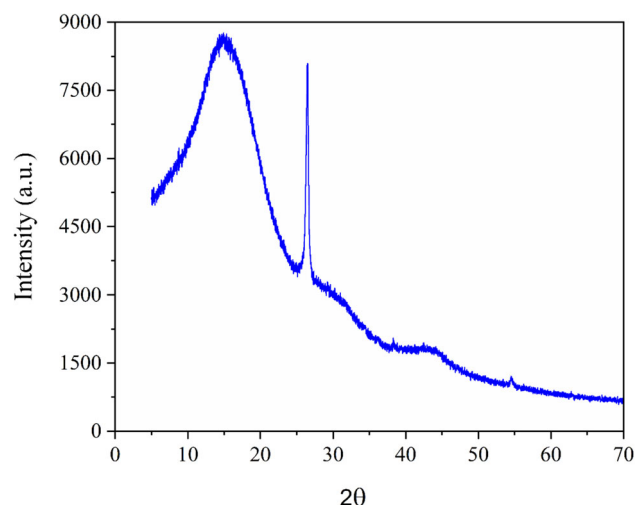


Fig. 5 XRD pattern of P(MPMESK 0.25-co-MMA)/NG 11 wt%

FT-IR spectra of the pure copolymer. FT-IR spectra of the partially degraded polymer at 340 °C (Fig. 6d) indicated peaks at 1803, 1757, and 1012 cm^{-1} (C = O and C–O–C symmetric and asymmetric stretching bands in the six-membered anhydride ring, respectively) which are typical of a six-membered anhydride ring structure obtained by intramolecular cyclization. Considerable increases in intensities of these bands in the C=O region in the copolymer structure were observed when the temperature increased to 380 °C. Important bands appeared at 1803 cm^{-1} and 1757 cm^{-1} for 380 °C (anhydride C=O stretching of the six-membered ring), as indicated in Scheme 2. Similar results were found for the decomposition of poly(methacrylic acid) (PMAA), which indicate the degradation stage corresponding to the conversion of PMAA to polymethacrylic anhydride (PMAN) [43–45]. The C=O stretching at 1660 cm^{-1} belongs to the ketone C=O group in the chalcon structure. The intensity of this band decreased due to increased elimination of the chalcon side group in the MPMESK unit in the copolymer system heated to 380 °C (Fig. 6e). The degradation of the copolymer system revealed 1,3-bis(4-methoxyphenyl)prop-2-en-1-one molecule, as shown in Scheme 2. The formation of 1,3-bis(4-methoxyphenyl)prop-2-en-1-one during the degradation of the copolymer also indicates a decrease in the ketone C = O band at 1660 cm^{-1} , as shown in Fig. 6e.

3.5 Kinetic Analysis

Representative TG curves corresponding to the four different heating rates 5, 10, 15, and 20 °C/min for the copolymer nanocomposite are presented in Fig. 7. With an increasing heating rate, the weight loss curves and peak temperatures of the homopolymer, copolymers, or polymer composite systems shift to higher values in the TGA measurements. In

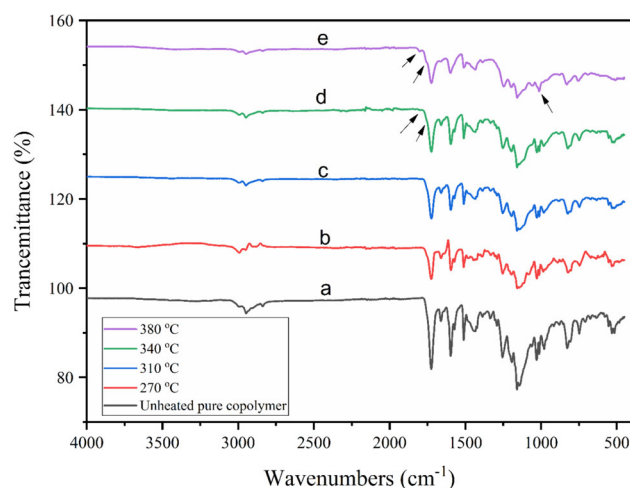


Fig. 6 FT-IR spectra of partially heated copolymer system: **a** unheated, **b** at 270 °C, **c** at 310 °C, **d** at 340 °C and **e** at 380 °C

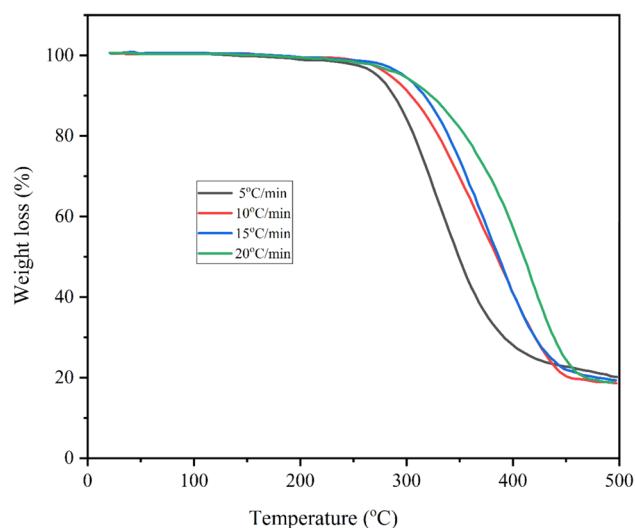


Fig. 7 TG curves for P(MPMESK 0.25-co-MMA)/NG 11 wt% nanocomposites under nitrogen atmosphere at different heating rates of 5, 10, 15, and 20 °C min⁻¹

general, degradation kinetic parameters are determined to understand the degradation process and the effect of fillers in composites on the polymer matrix, and to better describe the decomposition processes [46]. One of the most useful parameters is the effective activation energy [47, 48]. Therefore, to estimate the apparent activation energy and study the decomposition kinetics using the FWO method [49, 50] TG curves should be measured at least three times or more, and the heating rates should also be measured. One of the ICTAC kinetic project methods showed that isoconversion methods are best known because of the popularity of the KAS method [51]. The FWO and KAS methods are often used to determine the activation energy of material decomposition. In this



respect, the thermal analysis measurements of the nanocomposites were achieved at four different heating rates: 5, 10, 15, and 20 °C min⁻¹. A general pattern of the TG curves for a given weight loss is at a lower heating rate (5 °C min⁻¹) and decomposes at lower temperatures; however, at a higher rate (20 °C min⁻¹), it decomposes at higher temperatures.

Equation 1 is derived with other mathematical operations, including the Doyle approach used in the FWO method. The overall polymer degradation rate is usually described by Eq. 1.

$$\log(\beta) = \text{constant} - 0.457 \frac{E_a}{R.T} \quad (1)$$

T represents the temperature, β is the heating rate, and E_a is the activation energy. According to Eq. 1, if a plot of $\log\beta$ versus $1/T$ is linear, the activation energy E_a can be found from the slope of $0.457E_a/R$. The R (8.314 Jmol⁻¹ K⁻¹) is a constant.

In addition, activation energy values for thermal decomposition for P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposite can also be calculated using Eq. 2 and the KAS method. According to the KAS method, the activation energy is calculated from T , the temperature at which decomposition occurs at different heating rates.

$$\ln\left(\beta/T^2\right) = \ln[(AR/E_a g(\alpha))] - (E_a/RT) \quad (2)$$

Hence, the activation energy can be calculated from the linear dependence of $\ln\beta/T^2$ versus $1/T$ at various heating rates.

Figure 8a and b shows plots of $\log\beta$ against $1000/T$ (1/K) at various weight losses according to the FWO method and plots of $\ln\beta/T^2$ against $1000/T$ (1/K) at various weight losses according to the KAS method. The activation energies corresponding to different conversions were estimated from the slope of the lines of these plots. The activation energies from the FWO method, as shown in Fig. 8a, were estimated as 101.5, 82.8, 79.7, 73.9, 76.6, 79.4, and 110.3 kJ/mol at a conversion of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7, respectively. Additionally, the average activation energy value for conversion from 0.1 to 0.7 was estimated as 86.3 kJ/mol. Figure 8b shows the plots based on the KAS method for determining the activation energies, E_a , where the slopes of parallel-looking straight lines are considered equal to E_a/R . The parameters used and the results of E_a are listed in Table 2. Comparing the results of Table 2, activation energy values determined according to the FWO and KAS methods were found to be quite close.

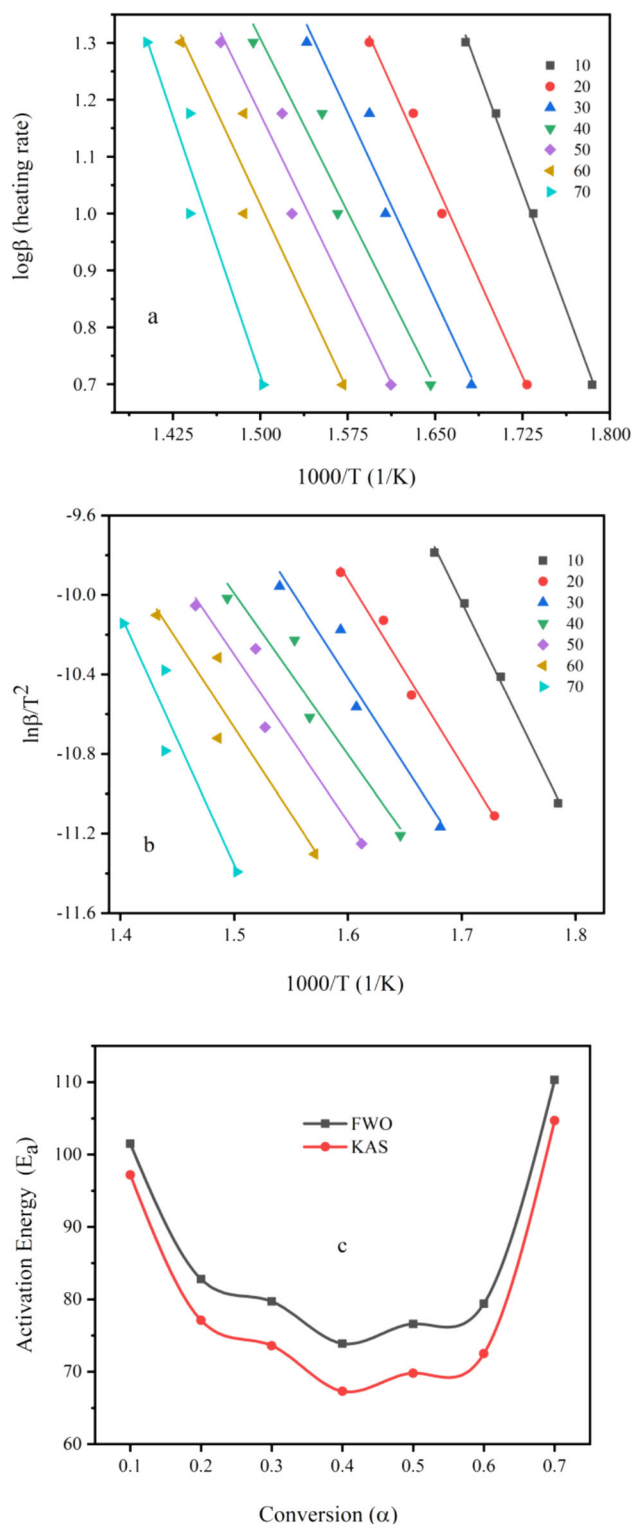


Fig. 8 a Plots of $\log\beta$ against $1000/T$ according to the FWO method for P(MPMESK 0.25-co-MMA)/NG 11 wt% nanocomposite; b plots of $\ln\beta/T^2$ against $1000/T$ according to the KAS method for P(MPMESK 0.25-co-MMA)/NG 11 wt% nanocomposite; c effective activation energy vs extent of degradation for the P(MPMESK0.25-co-MMA)/NG 11 wt% composite estimated using different isoconversional methods

Table 2 Activation energy values estimated with the FWO and KAS methods for P(MPMESK0.25-co-MMA)/NG 11wt%

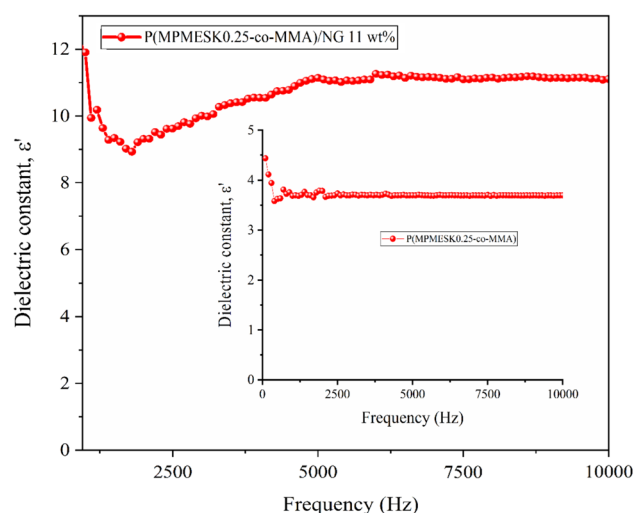
FWO method		KAS method	
Conversion/ α	Ea (kJ/mol)	Conversion/ α	Ea (kJ/mol)
0.10	101.5	0.10	97.2
0.20	82.8	0.40	77.1
0.30	79.7	0.30	73.6
0.40	73.9	0.40	67.3
0.50	76.6	0.50	69.8
0.60	79.4	0.60	72.5
0.70	110.3	0.70	104.7
Average	86.3	Average	80.31

3.5.1 Isoconversional Analysis

The FWO and KAS isoconversion analysis methods were carried out to correlate the dependence of the activation energy on the degree of decomposition. The activation energy change was investigated by considering the degree of dissociation and the limit range from $\alpha = 0.0$ to 0.70. The values of the activation energy, estimated by the FWO and KAS methods for the copolymer nanocomposite as a function of the extent of degradation, were compared with each other, as shown in Fig. 8c. The figure shows that the activation energy tends to be the same as the degree of decomposition. As mentioned before [52], the results of the two integral methods, namely the FWO and KAS methods, are considered similar to each other due to the large approximation; however, it is possible that results obtained with the differential methods can always shift to slightly higher values. It seems that degradation is characterized by first decreasing after increasing activation energy. E_a starts from near 101.5 kJ mol⁻¹ and decreases to 73.9 kJmol⁻¹ ($\alpha = 0.4$); it later increases to 110.3 ($\alpha = 0.7$) with the FWO method. The KAS method indicates an almost identical behavior. This is also an indication that degradation does not occur in one step. In this regard, as shown in Scheme 2, the formation of the six-membered anhydride structure in the copolymer structure above 340 °C and the formation of more than two degradation products due to the expectation that the anhydride structure will be decomposed at higher temperatures and the formation of a main chain backbone is correct.

3.6 Dielectric Measurements

Dielectric measurements of the pure copolymer and its composite were investigated at a frequency range of 100 Hz to 10 kHz. In the dielectric measurements, dielectric constant, ϵ' , dielectric loss factor, ϵ'' , and alternating conductivity, δ_{ac} ,

**Fig. 9** Variation of dielectric constant (ϵ') with frequency for **a** P(MPMESK 0.25-co-MMA) and **b** composite-loaded NG 11 wt%

were determined based on capacitance C_p , dissipation factor D , and resistance R_p parameter measurements. The dielectric constant, ϵ' , which is the real part of the complex dielectric permittivity, was calculated using Eq. 3 by measuring the capacitance at room temperature.

$$\epsilon' = C_p d / \epsilon_o A \quad (3)$$

where d is the thickness of the pellet, ϵ_o is the permittivity of free space, and A is the area of the pellet prepared under four tons of pressure. The variation of the ϵ' with frequency at room temperature for copolymer and polymer nanocomposite containing NG 11 wt% is shown in Fig. 9a and b, respectively. The ϵ' values of copolymer and P(MPMESK0.25-co-MMA)/NG 11 wt% at fixed temperature and 1 kHz were 3.52 and 9.4, respectively. It was found that the ϵ' at low frequency has higher values. However, as the frequency increases, the ϵ' decreased, which means that higher value of ϵ' at low frequency is due to contribution of space charge and electronic polarization [53]. The ϵ' of P(MPMESK0.25-co-MMA) was found to be around 3.5 at room temperature and 1 kHz, as indicated in Fig. 9a. Polymers have low dielectric constants and generally organic or inorganic electrically conductive fillers are introduced. Therefore, through this process, it becomes a polymeric material with a higher dielectric constant. Accordingly, NG 11 wt% was added to the polymer matrix to examine the effect of NG on the dielectric constant of the copolymer. As shown in Fig. 9b, the ϵ' of composite increased to 9.4. The NG in copolymer matrix causes induced interface or space charge polarization. This means that it is an increase in capacitance [54]. ϵ'' represents the imaginary part of the complex permittivity and indicates that some energy is dissipated due to charge transfer and molecular vibration due to the applied



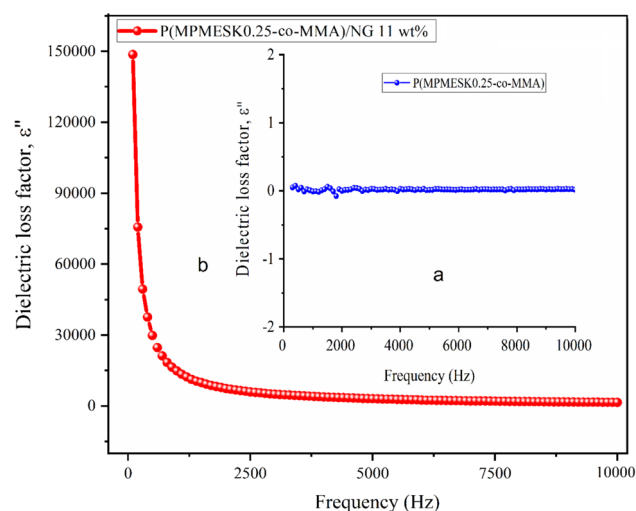


Fig. 10 Variation of dielectric loss factor (ϵ'') with frequency for **a** P(MPMESK0.25-co-MMA) and **b** composite-loaded NG 11 wt%

electric field effect. ϵ'' was calculated according to Eq. 4.

$$\tan \delta = \epsilon'' / \epsilon' \quad (4)$$

The variation of dielectric loss factor, ϵ'' , with frequency at room temperature for pure copolymer and polymer nanocomposites containing NG 11 wt% is compared and shown in Fig. 10a and b. The ϵ'' values of the copolymer are given in Fig. 10a and P(MPMESK0.25-co-MMA)/NG 11 wt% is shown in Fig. 10b at room temperature; at 1 kHz, it was found to be 0.15 and 14,500, respectively. As the frequency increased, ϵ'' of pure copolymer was found to be around 0.1, but ϵ'' of P(MPMESK0.25-co-MMA)/NG 11 wt% decreased exponentially. As shown in Fig. 10b, the ϵ'' values at 100 Hz, 1, 2, 5, and 10 kHz were 145,800, 14,500, 5800, 3520, and 1800. At high frequencies, ϵ'' exhibited a low value and remained constant. The dramatic decrease in dielectric loss of the polymer nanocomposite is related to the formation of a conducting percolation network of the conductive fillers in the polymer matrix. In designing an energy storage device, minimizing dielectric loss at a given dielectric constant is necessary. The frequency of ac conductivity σ_{ac} was determined from the observed resistance values for the film under examination.

The alternative conductivity σ_{ac} values were calculated from Eq. 5 using the R_p parameter.

$$\sigma_{ac} = d / R_p a \quad (5)$$

where d is the film thickness, R_p is the measured film resistance, and a is the cross-sectional area of the film. The ac conductivity satisfies the power law Eq. 6.

$$\sigma_{ac}(\omega) = A\omega^s \quad (6)$$

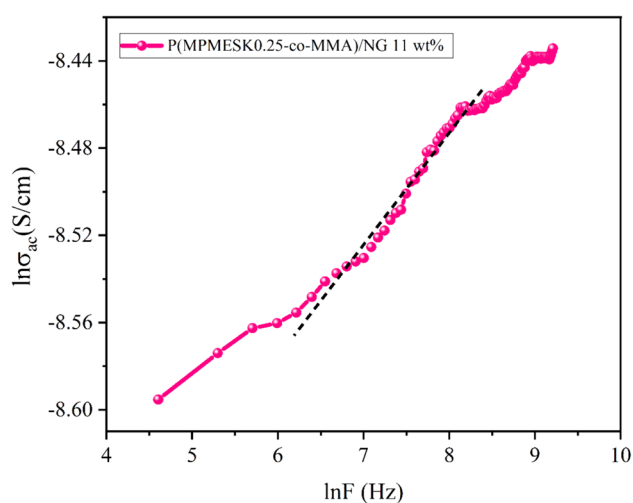


Fig. 11 Variation of $\ln \sigma_{ac}$ - $\ln F$ for P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposite

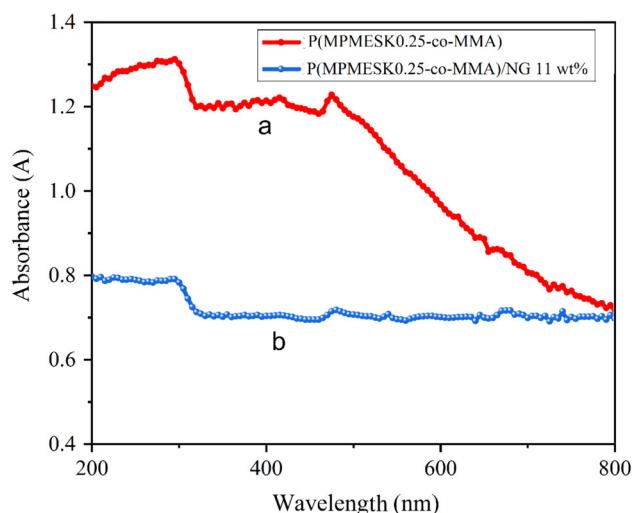


Fig. 12 Plot of absorbance versus wavelength for **a** pure copolymer and **b** copolymer-doped NG 11 wt%

where A is constant, ω is the angular frequency, and s is the fractional exponent. As shown in Fig. 11, s was calculated from the slope of the $\ln \sigma_{ac}$ versus $\ln F$ plot. The s value, $s = 0.05$, is less than 1, supporting the conclusion that the conduction mechanism of nanocomposite obeys the correlated barrier hopping (CBH) model [55]. In the CBH model, the charge carriers indicate hopping between regions over the potential barrier separating them. The inclusion of a Coulomb interaction between each barrier reduces the barrier height.

3.7 Optical Properties

Figure 12a and b indicates the variation of optical absorbance of P(MPMESK0.25-co-MMA) and P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposites with wavelength of the

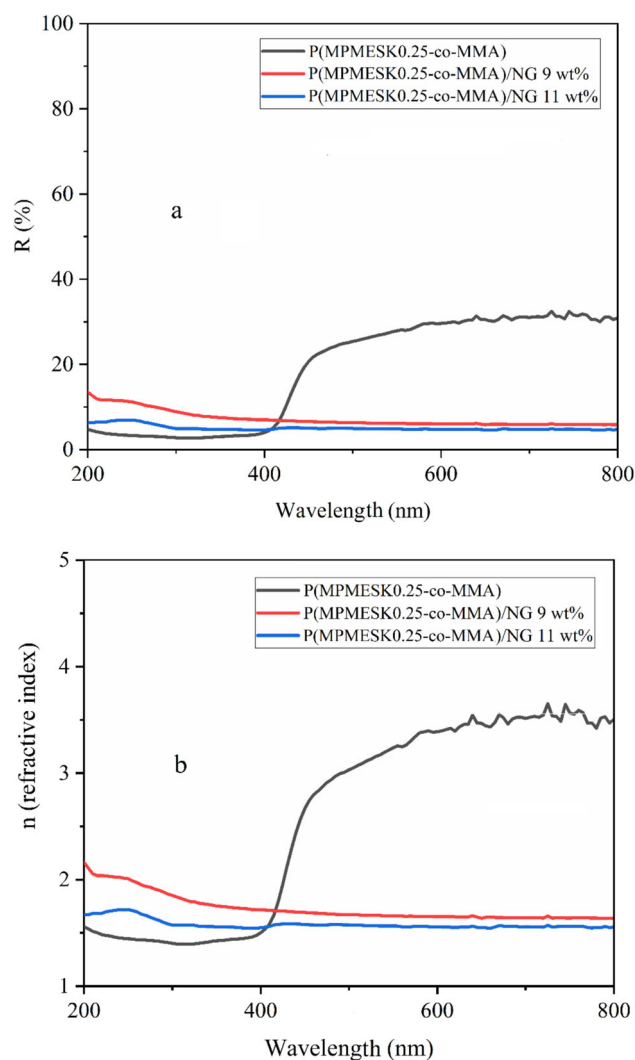


Fig. 13 Plot of **a** reflectance and **b** refractive index for the pure copolymer and its nanocomposites

incident light. The pure P(MPMESK0.25-co-MMA) indicated in Fig. 12a shows maximum absorbance at 295 nm. The max absorption bands at 295 nm observed in Fig. 12a and b are related to the n-p* transitions arising from the MPMESK units in the copolymer. However, the absence of the band above 295 nm in Fig. 12b indicates that NG particles block the UV above 300 nm and in the visible region. On the other hand, this behavior suggests that since the energy of the incident photons is absorbed by the NG, it does not have enough energy to interact with the atoms in the copolymer matrices [56].

The plots of the reflectance and refractive index of pure copolymer and its nanocomposites are shown in Fig. 13. Accordingly, Fig. 13a shows the reflectances of pure P(MPMESK0.25-co-MMA), P(MPMESK0.25-co-MMA)/NG 9 wt%, and P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposites. The reflectance of the pure

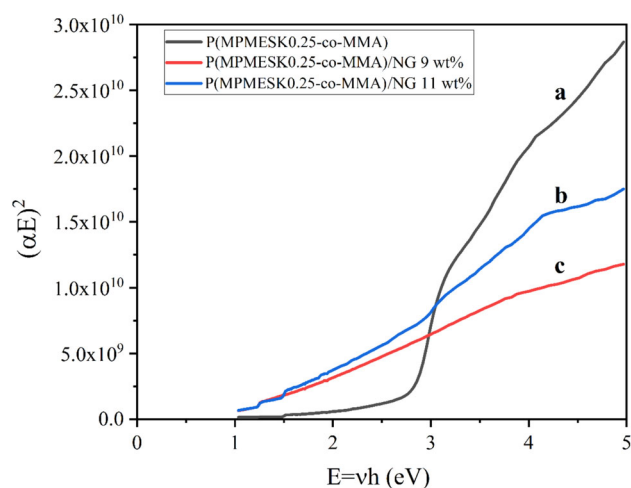


Fig. 14 Plot of $(\alpha E)^2$ versus $E = hv$ for pure copolymer and its composite systems: **a** P(MPMESK0.25-co-MMA)/NG, **b** P(MPMESK0.25-co-MMA)/NG 11 wt%, and **c** P(MPMESK0.25-co-MMA)/NG 9 wt%

P(MPMESK0.25-co-MMA) has considerably increased from 400 to 580 nm, and reflectance has not quite changed at a high wavelength. It decreased with increasing concentration of the NG nanoparticles in nanocomposites. The reflectance in the visible region decreased sharply after 400 nm, which represents the peak absorption of the NG nanoparticles. This behavior is clear in the high concentration of NG nanoparticles in the copolymer nanocomposites. The reduction of reflectance in the visible region is perhaps due to the absorption of the whole wavelength photons of the visible region. The refractive indexes of pure copolymer and its nanocomposites were measured and are shown in Fig. 13b. Refractive index is an important parameter for the design of optical systems. The measured refractive index of the pure copolymer is around 1.44 and almost changed at the UV region. After 392 nm, the refractive index of pure copolymer suddenly increases from 1.46 to 3.44 (630 nm). After 630 nm, it continues in a fixed or straight line. When copolymer matrix is loaded with NG 9 wt% and 11 wt%, the refractive indexes are considerably minimized and continue in a fixed or straight line in the visible region. That is, NG reasonably reduces the sensitivity of the copolymer to the visible region. This behavior also means that NG is a light stabilizer for the copolymer [57, 58].

The optical band gaps of pure copolymer and its composites were calculated using the E_g , absorption spectra and the Tauc relation (7).

$$\alpha_o nh = \alpha_o (hn - E_g)^n \quad (7)$$

Here, $h\nu$ is the photon energy, α_o is a constant and n is 1/2 for direct band semiconductors and 2 for indirect bands. Figure 14 demonstrates the relationship between $(\alpha_o hv)^2$ and the photon energy ($h\nu$) of P(MPMESK0.25-co-MMA)



and its nanocomposites. The optical energy gap of pure P(MPMESK0.25-co-MMA) (0 wt% NG) equals 2.73 eV. The optical energy gaps of P(MPMESK0.25-co-MMA) were 0.99 and 0.94 eV. These data clearly show that the optical energy band gap values depend on the weight percentage of the NG particles. As shown in Fig. 14, when the optical energy band gap of pure P(MPMESK0.25-co-MMA) and copolymer nanocomposite was compared, there was a decrease in the optical energy gap with an increasing NG amount. The energy gap was found to be inversely proportional to the weight percentage of the NG nanoparticles.

3.8 Current–Voltage Measurement

In order to understand the effect of the loaded NG on the electrical property of the composites, the electrical resistance of the composite depending on the content of NG 9 wt% and NG 11 wt% was investigated. The current–voltage (I–V) characteristic of copolymer/NG composites at room temperature is indicated in Fig. 15a. It was observed that the current increased with the applied voltage as the NG content in the polymer matrices increased. The charge carriers, i.e., electric dipoles produced due to space charge polarization, were oriented along the direction of the applied electric field. The higher conductivity occurring at 11 wt% of the NG is attributed to the compatibility between the copolymer matrix and NG, which is sufficient to obtain nanosized dispersions without any additional surface treatment. The nanocomposite containing NG 9 wt% showed linear behavior up to 10 V, while the nanocomposite containing NG 11 wt% showed linear behavior up to 2 V and exhibited nonlinear behavior at higher voltages. The nonlinear performance of materials is important as it enables various applications such as electro-optical fields [59]. From the current–voltage graph shown in Fig. 15a, the resistances of 9 and 11 wt% NG-doped composites were calculated as 3.15, and 1.78 k Ω , respectively.

3.9 dc Electrical Conductivity

Conducting polymer nanocomposites can be produced by adding conductive nanofillers such as NG, graphite, graphite oxide, MXene, and metal oxide into the polymer matrices. They have a specific electrical conductivity that indicates an increasing nonlinearly depending upon the increase of the nanofiller content [60]. When any conductive content, such as nanofiller, rises above the percolation threshold, the nanofillers form a conductive network in the polymer matrices, which significantly increases the electrical conductivity of the nanocomposites. Therefore, NG can act as an efficient inorganic phase for preparing conductive nanocomposites due to its good conductivity and favorable aspect ratio. NG is both thermally and electrically a good conductive inorganic material. NG's high thermal or electrical conductivity makes

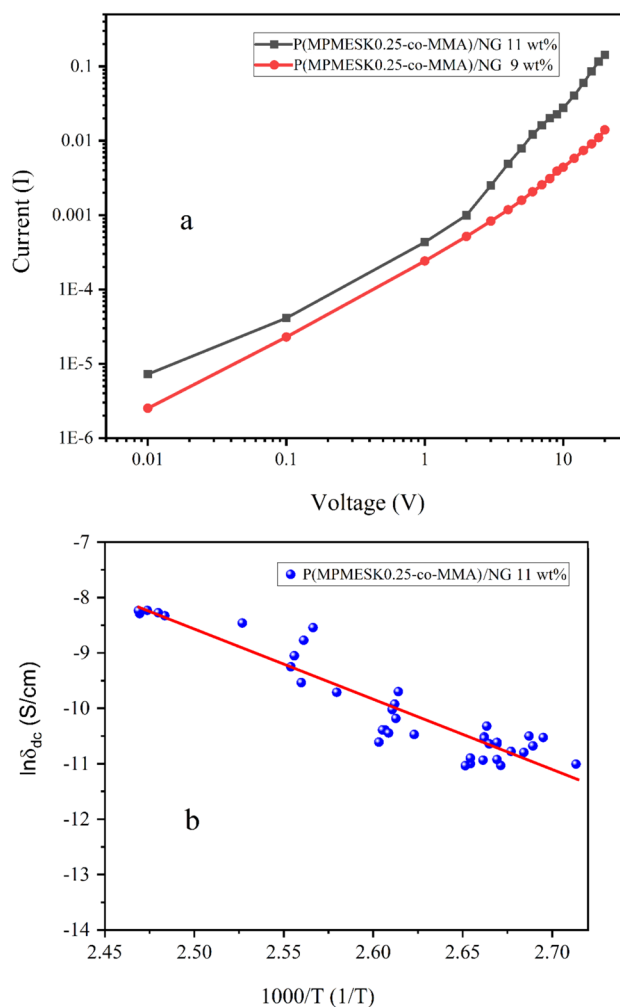


Fig. 15 **a** Graph of current versus voltage and **b** $\ln \sigma_{dc}$ versus $1/T$ for P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposite

it suitable for fabricating thermally conductive polymer composites [61]

The change in conductivity with temperature is one of the important measurements in investigating the conductivity properties of the prepared nanocomposite materials. To find the activation energy for the thermal activation processes, the Arrhenius Eq. (8) was used. A linear relation of $\ln \sigma_{dc}$ with $1/T$ indicates that the dc electrical conductivity follows the Arrhenius equation [62–64].

$$\sigma_{dc} = \sigma_o \exp(-E_g/kT) \quad (8)$$

where E_a is the activation energy under the dc field, σ_o is the pre-exponential factor, K is Boltzmann's constant, and T is the absolute temperature.

Figure 15b shows the variation of $\ln \sigma_{dc}$ versus $1/T$ as a function of temperature from (360–410 K) for P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposites.

The electrical conductivity behavior of some nanocomposite systems has revealed that dc conductivity will occur at a percolation threshold below 1.0 wt% for different filler content [65]. The percolation of the graphene filled composites was achieved at a 2.4% loading [66]. In order to determine the activation energy value from the temperature-dependent change of the dc electrical conductivity, it was calculated as 1.09 eV from the straight slope of the graph, obeying the Arrhenius Equation.

The activation energy corresponds to the energy required for transmission from one site to another. It was observed that the conductivity increased with increasing temperature. Therefore, the prepared nanocomposite can be said to have semiconductor behavior. On the other hand, this behavior indicates that the activation energy is positive, as it indicates that the carriers are more likely to move from the trap state to the mobile state. According to the percolation theory, energy activation decreased when the NG concentration increased, and conductivity increased because the NG particles formed a connected path through the copolymer matrices. P(MPMESK0.25-co-MMA)/NG 11 wt% exhibits higher increments in electrical conductivity compared to the P(MPMESK0.25-co-MMA)/NG 9 wt% composite.

4 Conclusions

The structure of the synthesized copolymer was characterized by ^1H -NMR spectroscopy. The copolymer/NG nanocomposites with two different concentrations of NG particles were successfully prepared. The morphology of the nanocomposite was studied using XRD and SEM techniques. The thermal stability of the pure copolymer and its nanocomposites was investigated with a TG instrument. Thermal stabilities of pure P(MPMESK0.25-co-MMA) and P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposites were higher than that of the neat copolymer. For example, with the addition of NG 11 wt% to pure P(MPMESK0.25-co-MMA), the initial decomposition temperature was different around 9 °C and the temperature at a weight loss of 11 wt% increased to around 26 °C. Therefore, adding NG to the copolymer matrix could significantly improve its thermal stability. Besides, the activation energies required for the thermal decomposition of P(MPMESK0.25-co-MMA)/NG 11 wt% nanocomposite were evaluated by both the FWO and KAS methods. The activation energies of thermal decomposition estimated according to the FWO method were similar to those obtained with the KAS method. Adding NG to the polymer matrices significantly increased the composite's dielectric constant and dielectric loss factor. The dc electrical conductivity σ_{dc} follows Arrhenius behavior, and the estimated activation energy value was 1.092 eV. In addition, the nanocomposite material exhibited semiconductor behavior.

The ac electrical conductivity σ_{ac} increased and supported the conformation of the nanocomposite's conduction mechanism to the CBH model. While the reflectance and refractive index of the pure copolymer did not change with increasing wavelength in the UV region, it increased significantly, especially at the beginning of the visible region, and this increase continued until 630 nm. However, when NG was added to the copolymer matrices, it significantly reduced and masked the pure copolymer's increased reflectance and refractive index between 400 and 630 nm. The optical energy band gap of the pure copolymer contains more value than its nanocomposites. As the NG content in the copolymer matrices increased, the optical energy band gap decreased from 2.73 to 0.94 eV.

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Declarations

Conflict of interest The authors report no potential conflict of interest.

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References

- Arvinte, A.; Sesay, A.M.; Virtanen, V.: Designing carbon reinforced PMMA composites for integrated electrodes as electrochemical detectors in PMMA microchips. *J. Electroanal. Chem.* (2020). <https://doi.org/10.1016/j.jelechem.2020.114486>
- Aziz, S.B.; Abdullah, O.G.; Brza, M.A.; Azawy, A.K.; Tahir, D.A.: Effect of carbon nano-dots (CNDs) on structural and optical properties of PMMA polymer composite. *Results Phys.* **15**, 102776 (2019). <https://doi.org/10.1016/j.rinp.2019.102776>
- Sanjay, V.; Rajashekara, K.M.; Johns, J.; Pattar, V.: The dielectric and impedance spectroscopy of poly vinyl alcohol doped with carbon (PVA-C). *Physica B* (2023). <https://doi.org/10.1016/j.physb.2022.414561>
- Kim, H.; Abdala, A.A.; Macosko, C.W.: Graphene/polymer nanocomposites. *Macromolecules* (2010). <https://doi.org/10.1021/ma100572e>
- Luo, H.; Wang, F.; Guo, R.; Zhang, D.; He, G.; Chen, S.; Wang, Q.: Progress on polymer dielectrics for electrostatic capacitors application. *Adv. Sci.* (2022). <https://doi.org/10.1002/adv.202202438>
- Zaidi, B.; Smida, N.; Althobaiti, M.G.; Aldajani, A.G.; Almdhaibri, S.D.: Polymer/carbon nanotube based nanocomposites for photovoltaic application: functionalization, structural, and optical properties. *Polymers* (2022). <https://doi.org/10.3390/polym14061093>



7. Alam, F.; Elsherif, M.; Salih, A.E.; Butt, H.: 3D printed polymer composite optical fiber for sensing applications. *Addit. Manuf.* (2022). <https://doi.org/10.1016/j.addma.2022.102996>
8. Sun, X.; Sun, H.; Li, H.; Peng, H.: Developing polymer composite materials: carbon nanotubes or graphene? *Adv. Mater.* (2013). <https://doi.org/10.1002/adma.201301926>
9. Shi, Z.; Chen, X.; Wang, X.; Zhang, T.; Jin, J.: Fabrication of super-strong ultrathin free-standing single-walled carbon nanotube films via a wet process. *Adv. Funct. Mater.* (2011). <https://doi.org/10.1016/j.tsf.2015.11.002>
10. Mamedov, A.A.; Kotov, N.A.; Prato, M.; Guldi, D.M.; Wicksted, J.P.; Hirsch, A.: Molecular design of strong single-wall carbon nanotube/polyelectrolyte multilayer composites. *Nat. Mater.* (2002). <https://doi.org/10.1038/nmat747>
11. Shim, B.S.; Zhu, J.; Jan, E.; Critchley, K.; Ho, S.; Podsiadlo, P.; Sun, K.; Kotov, N.A.: Multiparameter structural optimization of single-walled carbon nanotube composites: toward record strength, stiffness, and toughness. *ACS Nano* **3**, 1711–1722 (2009)
12. Friddle, R.W.; Lemieux, M.C.; Cicero, G.; Artyukhin, A.B.; Tsukruk, V.V.; Grossman, J.C.; Galli, G.; Noy, A.: Single functional group interactions with individual carbon nanotubes. *Nat. Nanotechnol.* (2007). <https://doi.org/10.1038/nnano.2007.334>
13. Grady, B.P.: Carbon nanotube-polymer composites: manufacture, properties, and applications, John Wiley & Sons Inc., Hoboken (2011). <https://doi.org/10.1002/9781118084380.fmatter>
14. Ekbote, A.N.; Maidur, S.R.; Jahagirdar, J.R.; Patil, P.S.; Soma, V.R.: Femtosecond nonlinear optical investigations of nitro chalcones-doped PMMA thin films for optical limiting and photonic applications. *Mater. Today Commun.* (2023). <https://doi.org/10.1016/j.mtcomm.2023.107240>
15. Siddiqui, V.U.; Ansari, A.; Khan, I.; Siddiqui, W.A.; Akram, M.K.; Khan, A.; Asiri, A.M.: Nanographene composite ion exchanger properties and applications. Woodhead Publishing. (2019). <https://doi.org/10.1016/B978-0-08-102509-3.00021-3>. (ISBN9780081025093)
16. Abbas, A.N.; Liu, B.; Narita, A.; Dössel, L.F.; Yang, B.; Zhang, W.; Tang, J.; Wang, K.L.; Räder, H.J.; Feng, X.; Müllen, K.; Zhou, C.: Vapor-phase transport deposition, characterization, and applications of large nanographenees. *J. Am. Chem. Soc.* (2015). <https://doi.org/10.1021/ja513207e>
17. Bagheri, H.; Shirzadmehr, A.; Rezaei, M.; Khoshshafar, H.: Determination of tramadol in pharmaceutical products and biological samples using a new nanocomposite carbon paste sensor based on decorated nanographene/tramadol-imprinted polymer nanoparticles/ionic liquid. *Ionics* (2018). <https://doi.org/10.1007/s11581-017-2252-1>
18. Zhao, X.; Jiaqiang, E.; Wu, G.; Deng, Y.; Han, D.; Zhang, B.; Zhang, Z.: A review of studies using graphenes in energy conversion, energy storage and heat transfer development. *Energy Convers. Manag.* (2019). <https://doi.org/10.1016/j.enconman.2019.01.092>
19. Bai, S.; Yang, L.; Haase, K.; Wolansky, J.; Zhang, Z.; Tseng, H.; Talnack, F.; Kress, J.; Andrade, J.P.; Benduhn, J.; Ma, J.; Feng, X.; Hamsch, M.; Mannsfeld, S.C.B.: Nanographene-based heterojunctions for high-performance organic phototransistor memory devices. *Adv. Sci.* (2023). <https://doi.org/10.1002/adv.202300057>
20. Zhang, X.; Zhang, H.; Li, C.; Wang, K.; Sun, X.; Ma, Y.: Recent advances in porous graphene materials for supercapacitor applications. *RSC Adv.* (2014). <https://doi.org/10.1039/c4ra07869a>
21. Burke, A.: Ultracapacitor technologies and application in hybrid and electric vehicles. *Int. J. Energy Res.* (2010). <https://doi.org/10.1002/er.1654>
22. Yu, G.; Xie, X.; Pan, L.; Bao, Z.; Cui, Y.: Hybrid nanostructured materials for high-performance electrochemical capacitors. *Nano Energy* (2013). <https://doi.org/10.1016/j.nanoen.2012.10.006>
23. Hall, P.J.; Mirzaei, M.; Fletcher, S.I.; Sillars, F.B.; Rennie, A.J.R.; Shitta-Bey, G.O.; Wilson, G.; Cruden, A.; Carter, R.: Energy storage in electrochemical capacitors: designing functional materials to improve performance. *Energy Environ. Sci.* (2010). <https://doi.org/10.1039/c0ee00004c>
24. Subramanian, K.; Krishnassamy, V.; Nanjundan, S.; Reddy, A.V.R.: Photosensitive polymer: synthesis, characterization and properties of a polymer having pendant photocrosslinkable group. *Eur. Polym. J.* (2000). [https://doi.org/10.1016/S0014-3057\(00\)00008-2](https://doi.org/10.1016/S0014-3057(00)00008-2)
25. Barim, G.; Altun, O.; Yayla, M.G.: Methacrylate polymers having pendant chalcone Moieties: monomer reactivity ratios, thermal and optical properties. *Polymer (Korea)* (2015). <https://doi.org/10.7317/pk.2015.39.1.13>
26. Selvam, P.; Babu, K.V.; Penlidis, A.; Nanjundan, S.: Studies on photocrosslinkable copolymers of 4-methacryloyloxyphenyl-3', 4'-dimethoxystyryl ketone and methyl methacrylate. *Euro. Polym. J.* **41**(4), 831–841 (2005). <https://doi.org/10.1016/j.eurpolymj.2004.10.049>
27. Sharif, F.; Arjmand, M.; Moud, A.A.; Sundararaj, U.; Roberts, E.P.: Segregated hybrid poly (methyl methacrylate)/graphene/magnetite nanocomposites for electromagnetic interference shielding. *ACS Appl.* (2017). <https://doi.org/10.1021/acsami.6b13986>
28. Abdollahi, H.; Najafi, V.; Amiri, F.: Determination of monomer reactivity ratios and thermal properties of poly (GMA-co-MMA) copolymers. *Polym. Bull.* **78**, 493–511 (2021). <https://doi.org/10.1007/s00289-020-03123-5>
29. Zhang, W.; Zhang, K.; Wang, Y.; Du, L.; Liu, R.; Zhu, J.; Zhang, C.; Zhang, G.: Exploring the impact of poly (sodium styrene sulfonate) dispersants' architecture on their performance in coal water slurry preparation. *J. Mol. Liq.* (2024). <https://doi.org/10.1016/j.molliq.2024.126140>
30. Teramachi, S.; Hasegawa, A.; Akatsuka, M.; Yamashita, A.; Take-moto, N.: Synthesis and characterization of polymeric schiff bases and their metal chelates. *Macromol.* (1978). [https://doi.org/10.1016/0014-3057\(92\)90294-C](https://doi.org/10.1016/0014-3057(92)90294-C)
31. Coskun, M.; Barim, G.; Demirelli, K.: Thermal stabilities of poly(n-acryloyl-n'-methylpiperazine), its blends with poly(methyl methacrylate), and poly(n-acryloyl-n'-methylpiperazine-co-methyl methacrylate). *J. Macromol. Sci. Chem. A.* (2006). <https://doi.org/10.1080/10601320500405950>
32. Bergeret, A.; Alberola, N.: A Study of the interphase in styrene methacrylic acid copolymer/glass bead composites. *Polymer* (1996). [https://doi.org/10.1016/0032-3861\(96\)87639-7](https://doi.org/10.1016/0032-3861(96)87639-7)
33. Marazzato, C.; Peneva, Y.; Lefterova, E.; Filippi, S.; Minkova, I.: Kinetics of nonisothermal degradation of nanocomposites based on functionalized polyethylenes. *Polym. Test.* (2007). <https://doi.org/10.1016/j.polymertesting.2007.01.006>
34. Cheng, H.K.F.; Sahoo, N.G.; Pan, Y.; Li, L.; Chan, S.H.; Zhao, J.; Chen, G.: Complementary effects of multi-walled carbon nanotubes and conductive carbon black on polyamide 6. *J. Polym. Sci.* (2010). <https://doi.org/10.1002/POLB>
35. Sahoo, N.G.; Cheng, H.K.F.; Cai, J.; Li, L.; Chan, S.H.; Zhao, J.; Yu, S.: Improvement of mechanical and thermal properties of carbon nanotube composites through nanotube functionalization and processing methods. *Mater. Chem. Phys.* (2009). <https://doi.org/10.1016/j.matchemphys.2009.06.007>
36. Tjong, S.C.; Ba, S.P.: Mechanical behaviors of polypropylene/carbon nanotubenano composites: the effects of loading rate and temperature. *Mater. Sci. Eng.* (2008). <https://doi.org/10.1016/j.jmse.2007.08.050>
37. Chieng, W.; Ibrahim, N.A.; Yunus, W.M.Z.W.; Hussein, M.Z.: Poly(lactic acid)/poly(ethylene glycol) polymer nanocomposites: effects of graphene nanoplatelets. *Polymers* (2014). <https://doi.org/10.3390/polym6010093>



38. Ghoshal, D.; Jain, R.; Koratkar, N.A.: Graphene's partial transparency to Van der Waals and electrostatic interactions. *Langmuir* (2019). <https://doi.org/10.1021/acs.langmuir.9b01887>
39. Chae, S.; Jang, S.; Choi, W.J.; Kim, Y.S.; Chang, H.; Lee, T.I.; Lee, J.O.: Lattice transparency of graphene. *Nano Lett.* **17**(3), 1711–1718 (2017). <https://doi.org/10.1021/acs.nanolett.6b04989>
40. Khabisi, M.A.; Roudini, G.; Barahuie, F.; Sheybani, H.; Ibrar, M.: Evaluation of phase change material-graphene nanocomposite for thermal regulation enhancement in buildings. *Heliyon* (2023). <https://doi.org/10.1016/j.heliyon.2023.e21699>
41. Batakliiev, T.; Georgiev, V.; Kalupgian, C.; Muñoz, P.A.; Ribeiro, H.; Fechine, G.J.; Andrade, R.J.; Ivanov, E.; Kotsilkova, R.: Physico-chemical characterization of PLA-based composites holding carbon nanofillers. *Appl. Compos. Mater.* **28**(4), 1175–1192 (2021). <https://doi.org/10.1007/s10443-021-09911-0>
42. Sembiring, H.; Sihotang, H.; Raja, S.L.; Supeno, M.; Pasaribu, N.; Simanjuntak, C.; Pratiwi, S.: Facile method to synthesize N-graphene nano sheets. *Orient. J. Chem.* (2018). <https://doi.org/10.13005/ojc/3404035>
43. Grant, D.H.; Grassie, N.: The thermal decomposition of polymethacrylic acid. *Polymer* (1960). [https://doi.org/10.1016/0032-3861\(60\)90020-3](https://doi.org/10.1016/0032-3861(60)90020-3)
44. Ho, B.C.; Lee, Y.D.; Chin, W.K.: Thermal degradation of polymethacrylic acid. *J. Polym. Sci. Part A: Polym. Chem.* **30**(11), 2389–2397 (1992)
45. Fyfe, C.A.; McKinnon, M.S.: Investigation of the thermal degradation of poly(acrylic acid) and poly(methacrylic acid) by high-resolution ¹³C CP/MAS NMR spectroscopy. *Macromolecules* (1986). <https://doi.org/10.1021/ma00161a021>
46. Liu, P.; Zhen, W.: Structure-property relationship, rheological behavior, and thermal degradability of poly(lactic acid)/fulvic acid amide composites. *Polym. Adv. Technol.* (2018). <https://doi.org/10.1002/pat.4327>
47. Vyazovkin, S.: Modification of the integral isoconversional method to account for variation in the activation energy. *J. Comput. Chem.* **22**(2), 178–183 (2001)
48. Peterson, J.D.; Vyazovkin, S.; Wight, C.A.: Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene). *Macromol. Chem. Phys.* **202**(6), 775–784 (2001)
49. Pramoda, K.P.; Chung, T.S.; Lui, S.L.; Oikawa, H.; Yamaguchi, A.: Characterization and thermal decomposition of polyimide and polyimide liquid crystalline polymers. *Polym Degrad Stabil.* (2000). [https://doi.org/10.1016/S0141-3910\(99\)00138-X](https://doi.org/10.1016/S0141-3910(99)00138-X)
50. Kissinger, H.E.: Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand.* (1956). <https://doi.org/10.6028/jres.057.026>
51. Kissinger, H.E.: Reaction kinetics in differential thermal analysis. *Anal. Chem.* (1957). <https://doi.org/10.1021/ac60131a045>
52. Demirelli, K.; Barim, E.; Tuncer, H.; Barim, G.; Abubakar, A.M.: Synthesis and characterization of N (2 acetyl benzofuran 3 yl) methacryl amide and ethyl methacrylate copolymer/graphite oxide composites and study of their kinetic and electrical properties. *Polym. Bull.* (2022). <https://doi.org/10.1007/s00289-021-03730-w>
53. Demirelli, K.; Barim, E.; Çelik, A.; Yegin, M.; Aksoy, Y.; Hanay, O.; Hasar, H.: Photoresponse, thermal and electrical behaviors of MXene-based polysulfone nanocomposite. *Polym. Bull.* (2024). <https://doi.org/10.1007/s00289-023-05121-9>
54. Nan, W.; Shen, Y.; Ma, J.: Physical properties of composites near percolation. *Annu. Rev. Mater. Res.* (2010). <https://doi.org/10.1146/annurev-matsci-070909-104529>
55. Elliott, S.R.: Ac conduction in amorphous chalcogenide and pnictide semiconductors. *Adv. Phys.* (1987). <https://doi.org/10.1080/00018738700101971>
56. Indolia, A.P.; Gaur, M.S.: Optical properties of solution grown PVDF-ZnO nanocomposite thin films. *J. Polym. Res.* (2013). <https://doi.org/10.1007/s10965-012-0043-y>
57. Abazari, R.; Sanati, S.; Nadafan, M.; Cordes, D.B.; Slawin, A.M.; Safin, D.A.; Liu, M.: Integration of open metal sites in an amino-functionalized Sm (III)–organic framework toward enhanced third-order nonlinear optical property. *Inorg. Chem.* (2024). <https://doi.org/10.1021/acs.inorgchem.4c03046>
58. Salehi, G.; Bagherzadeh, M.; Abazari, R.; Hajilo, M.; Taherinia, D.: Visible light-driven photocatalytic degradation of methylene blue dye using a highly efficient Mg–Al LDH@ g-C₃N₄@ Ag₃PO₄ nanocomposite. *ACS Omega* (2024). <https://doi.org/10.1021/acsomega.3c07326>
59. Pan, Y.; Sanati, S.; Nadafan, M.; Abazari, R.; Gao, J.; Kirillov, A.M.: Postsynthetic modification of NU-1000 for designing a polyoxometalate-containing nanocomposite with enhanced third-order nonlinear optical performance. *Inorg. Chem.* (2022). <https://doi.org/10.1021/acs.inorgchem.2c02709>
60. Singh, B.; Arya, Y.; Lahiri, G.K.; Indra, A.: Electronic structure modulation in Prussian blue and its analogs: progress and challenges in perspective of energy-related catalysis. *Coord. Chem. Rev.* (2025). <https://doi.org/10.1016/j.ccr.2024.216288>
61. Nika, D.L.; Pokatilov, E.P.; Askerov, A.S.; Balandin, A.A.: Phonon thermal conduction in graphene: role of Umklapp and edge roughness scattering. *Phys. Rev. B* (2009). <https://doi.org/10.1103/PhysRevB.79.155413>
62. Mondal, S.P.; Aluguri, R.; Ray, S.K.: Dielectric and transport properties of carbon nanotube-CdS nanostructures embedded in polyvinyl alcohol matrix. *J. Appl. Phys.* (2009). <https://doi.org/10.1063/1.3142296>
63. Idris, N.K.; Aziz, N.N.; Zambri, M.S.; Zakaria, N.A.; Isa, M.I.: Ionic conductivity studies of chitosan-based polymer electrolytes doped with adipic acid. *Ionics* **15**, 643–646 (2009). <https://doi.org/10.1007/s11581-009-0318-4>
64. Abdel-karim, A.M.; Salama, A.H.; Hassan, M.L.: Electrical conductivity and dielectric properties of nanofibrillated cellulose thin films from bagasse. *J. Phys. Org. Chem.* (2018). <https://doi.org/10.1002/poc.3851>
65. Shen, B.; Lu, D.D.; Zhai, W.T.; Zheng, W.G.: Synthesis of graphene by low-temperature exfoliation and reduction of graphite oxide under ambient atmosphere. *J. Mater. Chem.* (2013). <https://doi.org/10.1039/C2TC00044J>
66. Fang, M.; Wang, K.G.; Lu, H.B.; Yang, Y.: Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites. *J. Mater. Chem.* (2009). <https://doi.org/10.1039/B908220D>

