



## Biophysical Properties of Polymethyl Methacrylate Blended with Maleated Castor Oil Filled with Calcium Carbonates in the Micro and Nano Scales



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**T**HE biophysical properties of films prepared from polymethyl methacrylate (PMMA) blended with maleated castor oil (COMA) with composition 70/30 wt% filled with different concentrations of calcium carbonate ( $\text{CaCO}_3$ ) in the micro and nano scales have been studied. The prepared films were characterized through different techniques such as, thermo gravimetric analysis TGA, scanning electron microscope SEM, differential scanning calorimetry DSC, in addition to dielectric properties at range of frequency from 0.1 Hz to 5 MHz and temperature range from (30 to 90) °C. The data obtained for the two investigated systems indicate that the dielectric permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  increased by increasing either the concentration of the filler or the temperature. Results of the electrical conductivity  $\sigma$  indicated that COMA is recommended to be used for electrostatic dissipation applications. Moreover the enzymatic degradation of the prepared films indicates that the weight remaining decrease with increasing either the time of immersing or the concentration of the filler.

**Keywords:** Biophysical, Castor oil, Dielectric properties, Electrical conductivity  $\sigma$ , Enzymatic degradation.

### Introduction

The incorporation of the fillers in the polymer matrix often exhibits remarkable improvement of mechanical, thermal and physico-chemical properties. In recent years, it has been found that layered silicate filled polymer composites often exhibit remarkable improvement of such properties when compared with pure polymer and their conventional microcomposite [1].

The effect of micro and nano particle size of calcium carbonate  $\text{CaCO}_3$  on thermal stability and melt rheology behavior of poly (lactic acid) (PLA) was investigated [2]. They found that, Artificial reinforcement filler for polymeric composite insulation for high voltage outdoor application was prepared. The possibility of waste material as filler for polymeric composite insulation that

beneficial to our environment and economy was studied. For such composite, a seashell ( $\text{CaCO}_3$ ) and waste glass ( $\text{SiO}_2$ ) were selected to produce an artificial wollastonite (calcium silicate- $\text{CaSiO}_3$ ) that use as filler and Polypropylene (PP) was utilized as a matrix. X-ray diffraction (XRD) technique was applied to reveal the chemical composition of an artificial wollastonite (AW) [3].

Thermal properties of composites synthesized from phenyltrimethoxysilane (PTMS) and potassium-montmorillonite (K-MMT) by using sol-gel technique were examined by using differential scanning calorimeter (DSC) to be used as new flame-retardant compounds [4].

The dielectric and mechanical properties of polystyrene (PS) acrylonitrile-butadiene rubber (NBR) blends were studied with the aim

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of improving the insulation properties of NBR. The effect of the addition of three types of fillers (quartz, talc, and calcium carbonate) was studied in increasing quantities (up to 80 phr) on the dielectric and mechanical properties. The variation of the dielectric properties with temperature (20 to 60)°C was also investigated [5]. The effect of different modified nano-CaCO<sub>3</sub> content on the compressive properties of epoxy resin cast and its carbon fibre composites was evaluated [6].

Novel abrasion-resistant nanocomposites based on poly (methyl methacrylate) (PMMA) as matrix and calcium carbonate (CaCO<sub>3</sub>) nanopowder as a filler have been prepared by an in situ polymerization process. The influence of nanopowders on the chemical–physical properties of the polymeric matrix has been investigated by performing thermal, morphological and mechanical analysis. The mechanical properties of nano-CaCO<sub>3</sub> particles-reinforced PVC were investigated [7]. PMMA/expanded graphite (EG) composites were prepared by direct solution blending of PMMA with the expanded graphite filler. Electrical conductivity and dielectric properties of the composites were measured by a four-point probe resistivity determiner and a dielectric analyzer (DEA) and compared with conventional PMMA/carbon black. The improvements in both electrical conductivity and structural integrity were attributed to the difference in filler geometry and the formation of conductive networks in the composites [8].

Some biopolymers like polysaccharides have poor mechanical properties, nanoparticles were incorporated in the polymer matrix to improve its mechanical, thermal stability and degradability to be used as packaging material [9]. Biodegradability characteristics of prepared films by blending dehydrated castor oil epoxy (DCOE) with poly (methyl methacrylate) (PMMA) and poly (methacrylic acid) (PMAA) are studied [10]. The aim of this work is to improve the biophysical properties of polymethyl methacrylate by blending with maleated castor oil (COMA) filled with micro and nano scales of calcium carbonate to be used for insulation purposes in addition to other biological applications.

## **Materials and Experimental Techniques**

### *Materials*

The materials used in this study are castor oil and soybean oil were obtained from ABCO Chemie, Gillingham, England. Maleic anhydride, succinic acid, 1,2-propanediol, Hydroquinone

and N,N-dimethyl benzylamine were obtained from Merck, Darmstadt, Germany. Tetrabutyl titanate, Ti (OBU)<sub>4</sub>, as the transesterification catalyst was reagent grade from Sigma- Aldrich, Steinheim, Germany. Polymethyl methacrylate (PMMA) with M.W.120000 (GPC) was obtained from Polyscience, Inc. Warrington, PA 18976. Chloroform with MW.119.38 obtained from New Delhi-11020 (INDIA). Buffer Solution PH 7.00 ± 0.05 (20 °C), LAB-SCAN was obtained from Portland. Enzyme lipase obtained from biocatalysts limited Cefn coed, Parc Nantgarw, Wales, CF 157QQ, United Kingdom. The enzyme activity is 52000 u/g. Calcium carbonate anhydrous CaCO<sub>3</sub> supplied from [HAS HMRZEL laboratories LTD. Netherlands while Nano calcium carbonate supplied from [Shandong Taian in China, Model number NPCCA series.

### *Experimental techniques*

#### *Synthesis of maleated castor oil (COMA)*

COMA was prepared by the reaction of castor oil (CO) with maleic anhydride (MA) at mole ratio 1:3. Castor oil 92.5 g, maleic anhydride 29.4 g and 0.012 wt% hydroquinone were mixed in a three-necked round-bottom flask equipped with a glass stirrer and a thermometer. The reaction proceeded with continuous stirring in an oil bath and the mixture was heated to 90 °C. When the maleic anhydride melted, 0.12 wt% of N,N-dimethyl benzyl amine was added and the reaction temperature was stabilized at 98 °C. The mixture was agitated at this temperature for 5 h. The product obtained was a light yellow, viscous liquid at room temperature.

#### *Preparation of the blends*

The polymer blends were prepared by solvent casting using chloroform solutions with a total polymer concentration of 5 wt%. The volume of each component solution (COMA and PMMA) was calculated to obtain film of 0.3 mm thickness. These components were mixed together for one hour, under magnetic stirring. The mixed solutions were then poured into Petri dishes and chloroform was slowly evaporated under ambient conditions. The resulting films were dried at 37 °C for 48 hours. The blend ratios were (100/0, 90/10, 80/20, 70/30, 60/40 and 50/50) wt%.

#### *Preparation of the composites*

Polymer blends of ratio 70/30 wt% were prepared by the same previous steps. Different weights of micro and nano Calcium Carbonate were added before stirring to obtain different

concentrations of the filler in the blend, (3, 5, 7, 10, 15, 20, 30, 40 & 50) wt% for  $\text{CaCO}_3$  in the microscale and (3, 5, 7, 10, 15 & 20) wt% for the nano scale.

#### *Biodegradation measurements*

The enzymatic degradation in phosphate buffer solution for 7 days was studied by weight loss method using the following equation:

Weight loss % =  $[(W_0 - W_t) / W_0] \times 100$ -----[1]  
where  $W_t$  is the weight after degradation and  $W_0$  is the initial weight.

Weight remaining % =  $(100 - \text{weight loss}) \%$ .....[2]

#### *Transmission Electron Microscope TEM*

The particle size of calcium carbonate powder filler was determined using Transmission Electron Microscope model: JEM-HR 2100 and accelerating voltage 200 kV. Japan.

#### *Scanning Electron Microscope SEM*

Scanning electron microscope (SEM) MODEL-163-JSM-T20 JEOL, Japan, was used to characterize the prepared polymer blends morphology. The samples were coated with a very thin layer of gold to avoid electrostatic charging during examination.

#### *Thermo Gravimetric Analysis TGA and Differential Scanning Calorimetry DSC*

TGA was performed using Perkin-Elmer, TGA 7 (USA) instrument. The rate of heating was 10 °C/ min up to 700 °C under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were carried out (by Frau Asbach, Section of Calorimetry, Uni. Ulm, Germany) using a DSC 2 - Perkin - Elmer. The heating rate used is 10 K/min.

#### *Dielectric measurements*

In the present study, dielectric and conductivity measurements were carried out by means of high-resolution broadband impedance analyzer (Schlumberger Solartron 1260). The frequency range of the applied ac electric field was between 0.1 Hz and 5 MHz. Good electromagnetic shielding was implemented to the whole sample holder in order to diminish noise problems that are common especially at low frequencies. The measurements were automated by interfacing the impedance analyzer with a personal computer through a GPIB cable IEE488. A commercial interfacing and automation software Lab VIEW was used for acquisition of data. The error in  $\epsilon'$  and  $\epsilon''$  amounts to 1% and 3%, respectively. The temperature of the samples was controlled by a temperature regulator with Pt 100 sensor. The error in temperature measurements amounts 0.5 °C. To avoid moisture, the samples were stored in desiccators in the presence of silica gel. Thereafter the sample was transferred to the measuring cell and left with  $\text{P}_2\text{O}_5$  until the measurements were carried out.

### **Results & Discussions**

#### *Transmission Electron Microscope TEM*

The biophysical properties of films prepared from polymethyl methacrylate (PMMA) blended with maleated castor oil (COMA) with composition 70/30 wt% filled with different concentrations of calcium carbonate ( $\text{CaCO}_3$ ), from 3-50 wt% in the micro scale and 3-20 wt% in the nano scales were studied. The ratio 70/30 wt% was chosen as the miscibility between PMMA and COMA is maximum [11]. The particle size of such fillers was investigated using TEM as in Fig. 1(a&b). It is about 1.79  $\mu\text{m}$  for  $\text{CaCO}_3$  in the micro scale and 55 nm in the nano scale

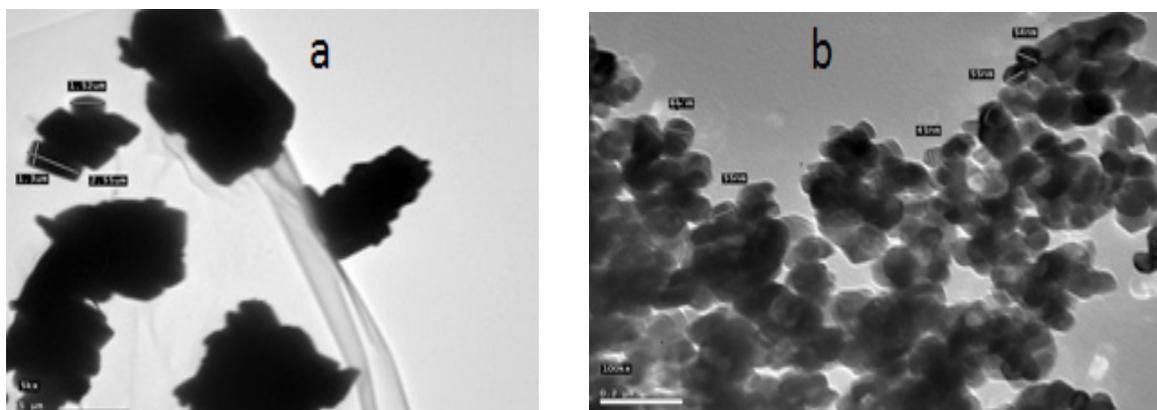


Fig. 1(a&b). Particle size of  $\text{CaCO}_3$  in (a) microscale (b) nano scale.

*Thermo gravimetric analysis (TGA)*

Thermal degradation of PMMA/COMA blend filled with different concentrations of  $\text{CaCO}_3$  in the micro and nano scales was studied by determining the weight loss during heating. Figure 2 shows the graphs for 0, 10, 20 and 40 wt%  $\text{CaCO}_3$  in the micro scale and 0, 10 and 20 wt%  $\text{CaCO}_3$  in the nano scale. Tables (1a and 1b) show detailed summary variation of 10, 25, 50 and 75 weight loss wt% of the investigated samples. It is observed that the initial degradation temperature at 10 wt% weight

loss of concentration 0 and 10 wt% is found to be faster than concentrations (20 and 40) wt%. As the concentration of the filler increases the degradation temperature will increase and shifts toward higher values. It is observed that thermal degradation occurs in two degradation steps, the first step for PMMA/COMA while the second step for  $\text{CaCO}_3$  degradation. From the figure it is noticed that the addition of  $\text{CaCO}_3$  as a filler enhances thermal stability of the investigated polymer blends in both micro and nano scale.

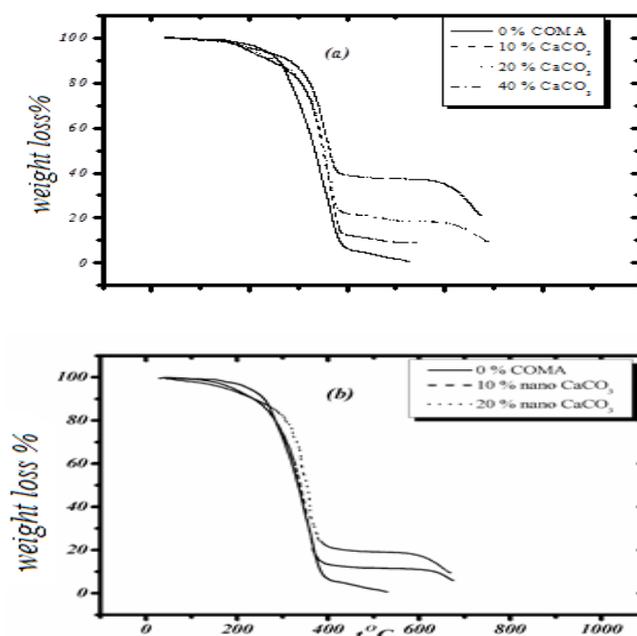


Fig. 2. TGA for COMA blend filled with different concentrations of  $\text{CaCO}_3$  (a)micro (b) nano.

TABLE (1a). TGA of PMMA/COMA blend filled with different concentrations of  $\text{CaCO}_3$  in the micro scale.

Sample PMMA/COMA wt%	Temp. at characteristic weight loss °C			
	10 %	25 %	50 %	75 %
0 %	242.23	254.45	324.81	359.86
10 %	242.29	318.80	351.00	371.07
20 %	251.18	321.10	353.00	380.17
40 %	280.88	333.75	364.04	656.55

TABLE (1b). TGA of PMMA/COMA blend filled with different concentrations of  $\text{CaCO}_3$  in the nano scale.

Sample PMMA/COMA wt%	Temp. at characteristic weight loss °C			
	10 %	25 %	50 %	75 %
0 %	242.23	254.45	324.81	359.86
10 %	242.30	318.00	351.00	371.00

*Scanning electron microscopy (SEM)*

The edge morphology of PMMA/COMA blend filled with different concentrations of  $\text{CaCO}_3$  in the micro and nano scales was investigated through SEM. Figures 3 and 4 show the graphs for 7, 20, 30 and 40 wt%  $\text{CaCO}_3$  in the micro scale and 5, 10, 15 and 20 wt%  $\text{CaCO}_3$  in the nano scale. These figures indicate that calcium carbonate is uniformly distributed in

the blend matrix. The light phase corresponds to calcium carbonate incorporated through the black phase of blend matrix attaining its saturation at 30 and 10 wt% in case of micro and nano  $\text{CaCO}_3$  respectively. The appearance of the large aggregates at higher concentrations of the filler could be ascribed to the filler-filler interaction rather than the filler-polymer interaction achieved at the lower concentrations.

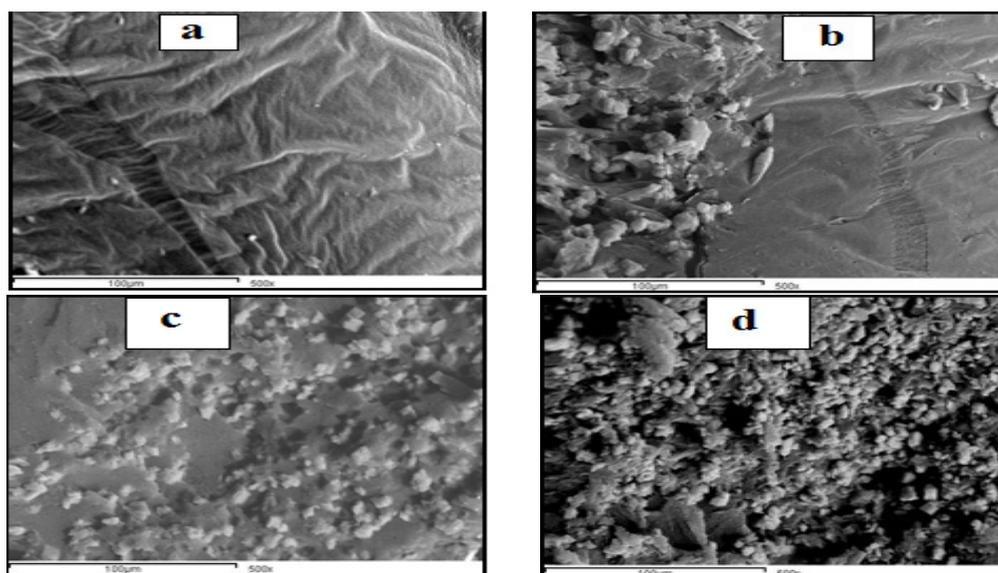


Fig. 3. Scanning electron microscopy for PMMA/COMA blend filled with different concentration of  $\text{CaCO}_3$  (a) 7 (b) 20 (c) 30 and (d) 40 wt% respectively at room temperature  $\sim 30^\circ\text{C}$ .

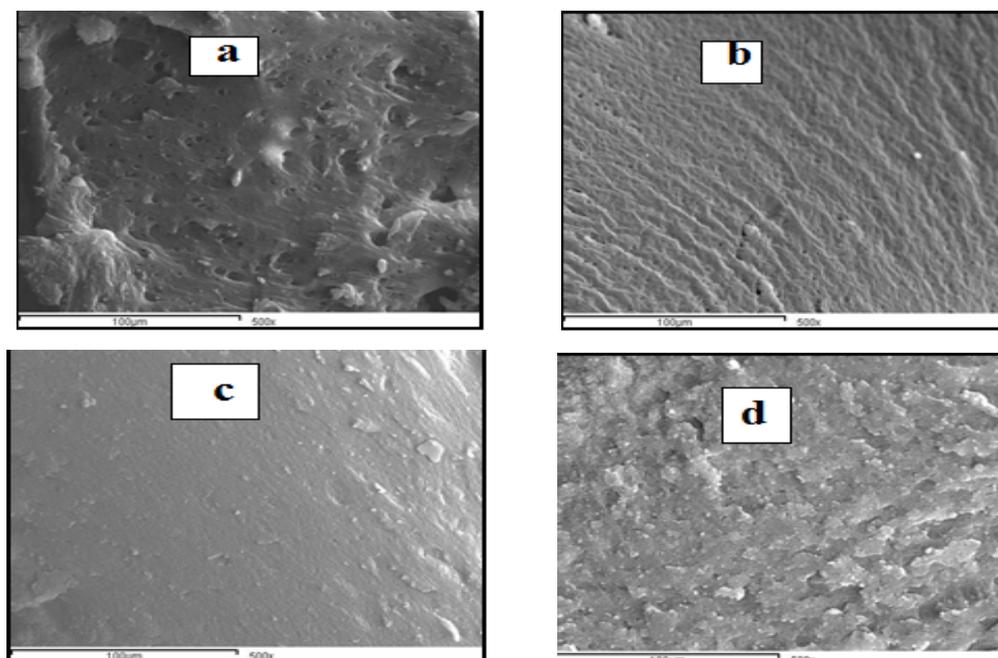


Fig. 4. Scanning electron microscopy for PMMA/COMA blend filled with different concentrations of nano  $\text{CaCO}_3$  (a) 5 (b) 10 (c) 15 and (d) 20 wt% respectively at room temperature  $\sim 30^\circ\text{C}$ .

### Differential scanning calorimetry (DSC)

The glass transition temperatures were measured calorimetrically for the studied samples COMA blended with PMMA and that filled with 20 wt % micro  $\text{CaCO}_3$  as white filler using (DSC) with heating rate  $10\text{ }^\circ\text{C}/\text{min}$  [12]. Examples of the

investigations are shown in Fig. 5. Figure (5-a) shows the glass transition temperature for PMMA/COMA blend ( $45.26\text{ }^\circ\text{C}$ ) while Fig. 5-b shows the glass transition temperature for the blend filled with 20 wt %  $\text{CaCO}_3$  is ( $66.25\text{ }^\circ\text{C}$ ).

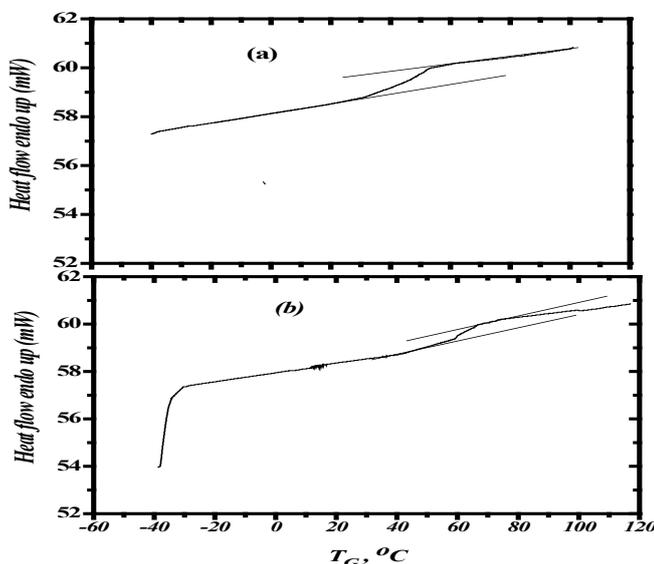


Fig. 5. The glass transition temperatures of (a) PMMA/COMA blend and (b) PMMA/COMA filled with 20%  $\text{CaCO}_3$ .

### Dielectric measurements

The dielectric permittivity  $\epsilon'$  and the dielectric loss  $\epsilon''$  of the prepared films were measured over a frequency range (0.1 Hz - 5 MHz) and temperature from 30 up to 90 °C. The data obtained indicate that  $\epsilon'$  and  $\epsilon''$  increased by increasing either the concentration of the filler or the temperature. Figures 6 and 7 illustrate the data of  $\epsilon'$  and  $\epsilon''$  obtained at 30 °C. The increase in  $\epsilon'$  and  $\epsilon''$  noticed by the addition of  $\text{CaCO}_3$  could be attributed to the presence of polar groups in the filler. As the filler loading increases, the density of the system is also increased and the extent of orientation of dipoles is retarded [13].

The decrease in  $\epsilon'$  noticed by increasing frequency shows an anomalous dispersion. This dispersion is accompanied by the relaxation mechanisms which are discussed in terms of the electric modulus  $M^*$  through the real and imaginary parts  $M'$  and  $M''$  according to equations.

$$M^* = M' + M'' \dots \dots \dots [3]$$

$$\text{where } M' = (\epsilon' / \epsilon'^2 + \epsilon''^2)$$

$$M'' = (\epsilon'' / \epsilon'^2 + \epsilon''^2).$$

$M'$  and  $M''$  were calculated for the whole investigated systems and the data obtained at 30

°C are illustrated graphically in Figures (6 and 7). The data of  $M''$  at the different frequencies have been analysed using computer program based on Havriliak Negami function [14].

The analyses revealed three relaxation times  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  characterizing the conductivity relaxation, segmental molecular motion and the local molecular motion associated to the group motions. Examples of the analyses are shown graphically in Fig. 8 for PMMA/COMA blend filled with 5 and 20 wt% in the nano scale at 30 and 80 °C respectively. The data obtained for the different relaxation times  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are illustrated graphically in Fig. 9 and 10 for the micro and nano  $\text{CaCO}_3$ . The decrease in  $\tau_1$  and  $\tau_2$  noticed by increasing either the filler content or temperature could be attributed to the increase in the conducting nature of the blend [15]. This decrease is found to be started sharply up to 60 °C after which a slight decrease is noticed. This could be attributed to the cooperative reorientation of the polymeric segments which expected to be happened through the glass transition temperature. The glass transition temperature range of the investigated systems is shown in Fig. 5. On the

other hand, the slight decrease noticed in  $\tau_1$  and  $\tau_2$  at concentrations 30 and 10 wt% in both micro and nano fillers could be attributed to the retardation of dipole orientation which is expected to be happened by the increase in the filler loading as the interaction between the polymer and the filler in the matrix becomes weak [16]. This finding is supported by the investigation carried out by SEM as shown in Fig. 3 and 4. The relaxation time  $\tau_3$  which ascribe the local molecular motions of the carbonyl group and related motions is found to

decrease by increasing temperature. This trend is similar to that found in case of  $\tau_1$  and  $\tau_2$ . On the other hand,  $\tau_3$  is found to increase by increasing the filler content up to concentrations 30 and 10 wt% of micro and nano fillers after which a sharp decrease has been noticed. This could be attributed to the steric hindrance which is expected to take place upon further increase in the filler content that partially contributes to decrease the group mobility.

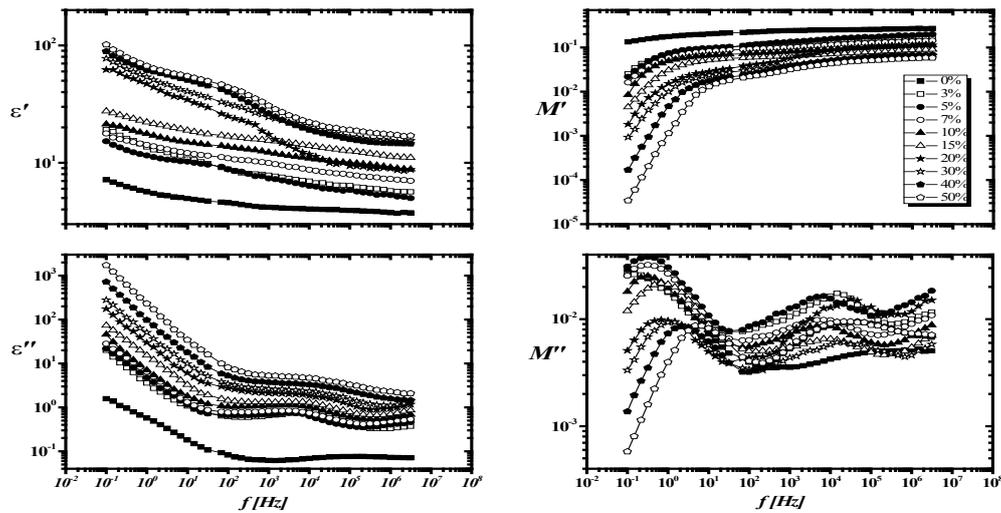


Fig. 6. Dielectric parameters ( $\epsilon'$  &  $\epsilon''$ ) and electric modulus ( $M'$  &  $M''$ ) as a function of frequency  $f$  for PMMA/COMA blends filled with different concentrations of CaCO<sub>3</sub> at temperature 30 °C.

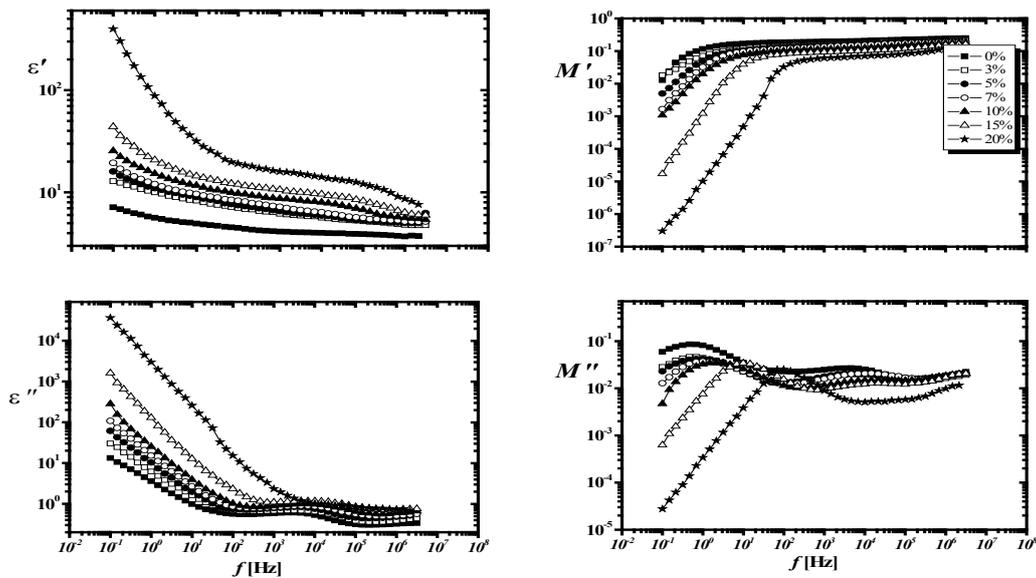


Fig. 7. Dielectric parameters ( $\epsilon'$  &  $\epsilon''$ ) and electric modulus ( $M'$  &  $M''$ ) as a function of frequency  $f$  for PMMA /COMA blends filled with different concentrations of nano CaCO room temperature ~30 °C.

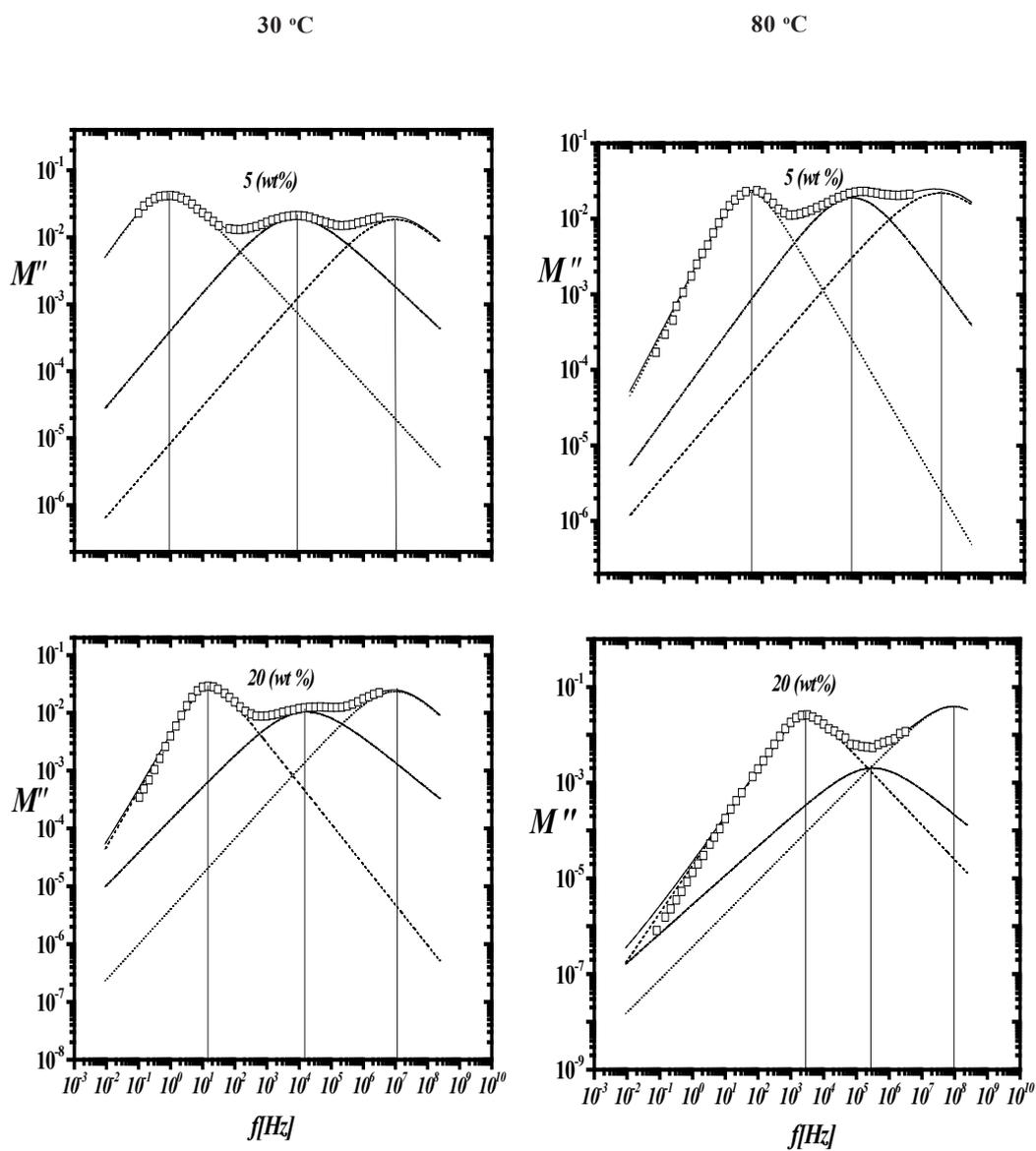


Fig. 8. Imaginary part of electric modulus  $M''$  as a function of frequency  $f$  for COMA filled with nano  $\text{CaCO}_3$  (5 and 20 wt %) at 30 °C and 80 °C. The experimental data are fitted using Havriliak-Negami function.

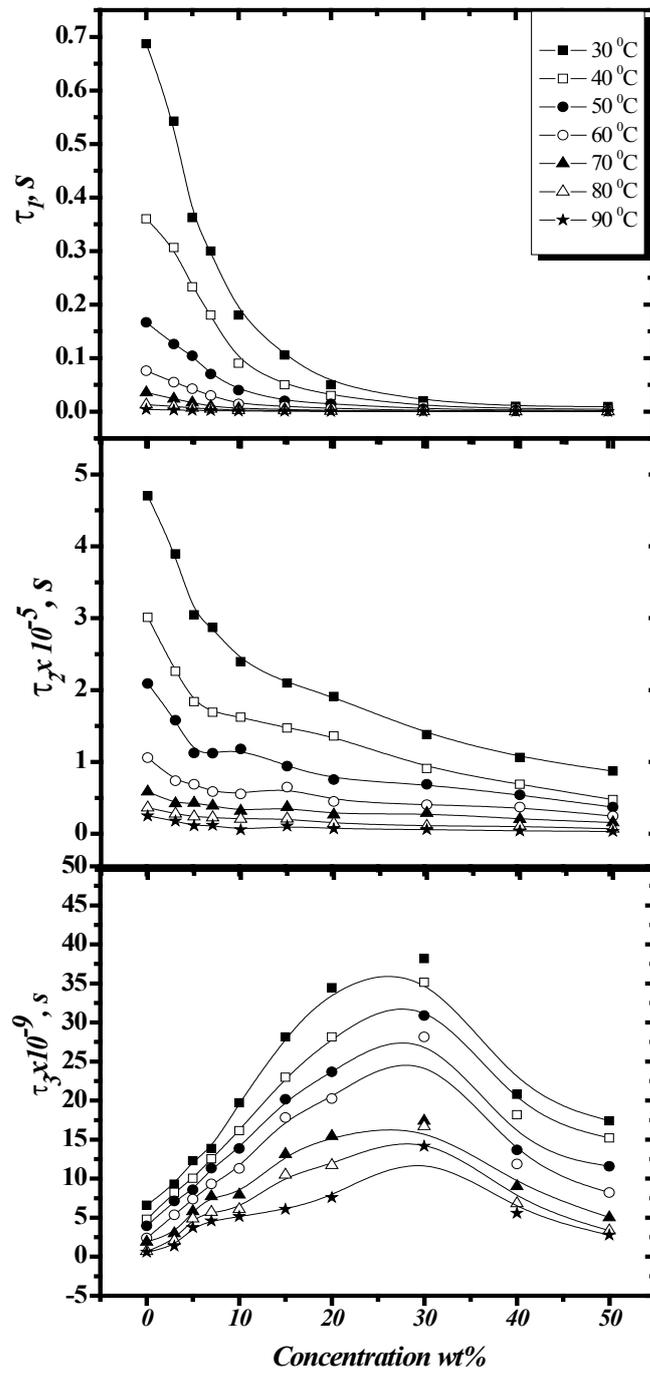


Fig. 9. Relaxation times ( $\tau_1$ ,  $\tau_2$  &  $\tau_3$ ) for PMMA/ COMA blend filled with different concentrations of  $\text{CaCO}_3$  at different temperatures ( $^{\circ}\text{C}$ ).

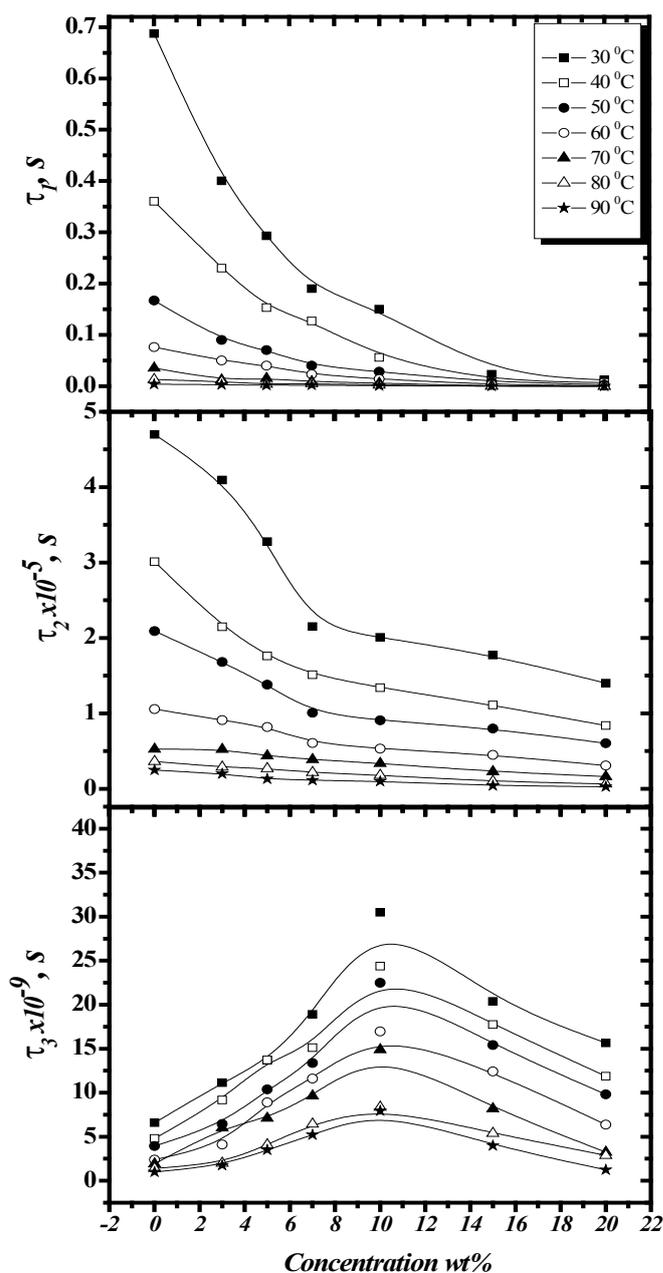


Fig. 10. Relaxation times ( $\tau_1, \tau_2, \tau_3$ ) for PMMA/ COMA blend filled with different concentrations of nano  $\text{CaCO}_3$  at different temperatures ( $^{\circ}\text{C}$ ).

#### Activation energy ( $E_{\tau}$ )

The temperature dependence of the relaxation times for the different relaxation mechanisms  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  are expressed by Arrhenius equation [17]. The data obtained for  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  for both investigated fillers are plotted graphically versus  $1000/T$ . Two straight lines below and above certain temperature  $\sim 60^{\circ}\text{C}$  are detected. From the slope of these lines, the activation  $E_{\tau}$  were calculated and illustrated graphically in Figures

(11 and 12). The two activation energies obtained for the whole investigated systems indicate that  $E_{\tau}$  after glass transition temperature is higher than that before glass transition temperature. This is considered to be a good support for the change which is expected to take place in the molecular behavior of the studied systems after the glass transition temperature as the main chain motion is usually frozen before such temperature.

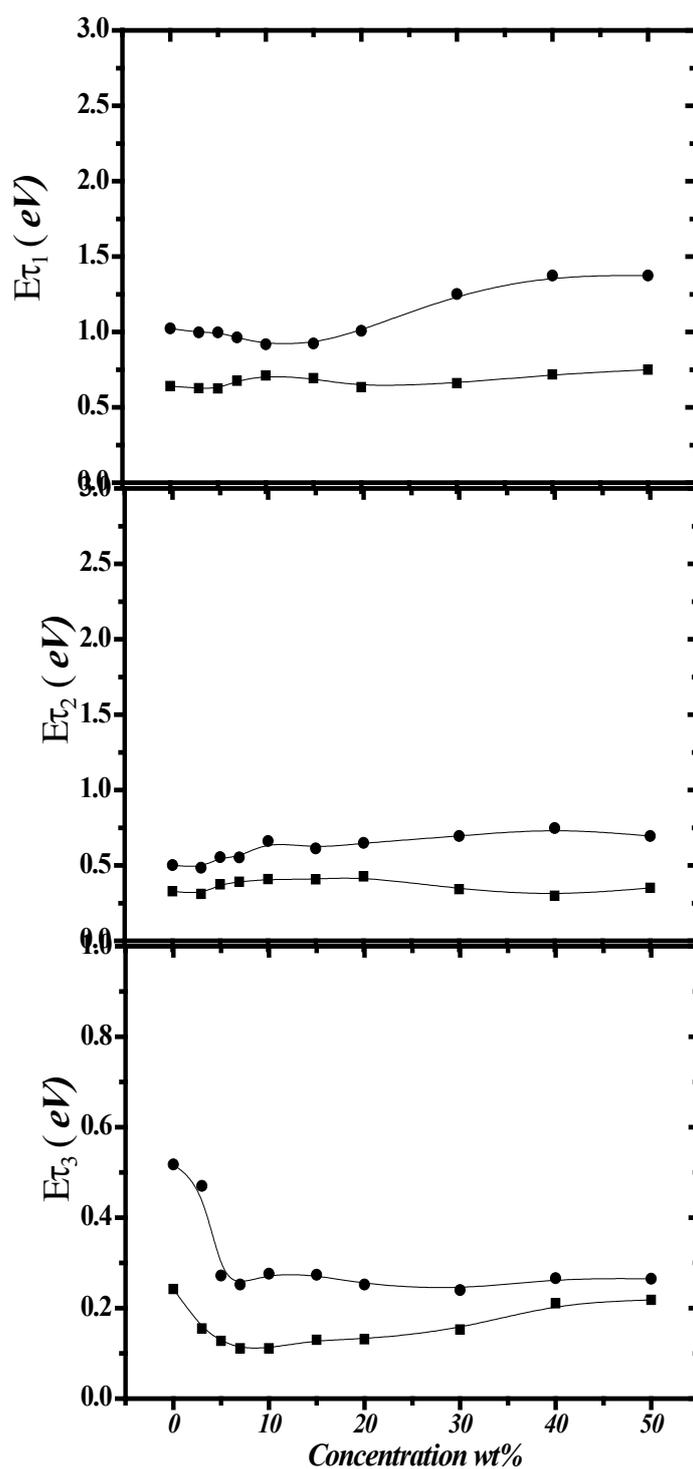


Fig. 11. Activation energies ( $E_{\tau_1}$ ,  $E_{\tau_2}$  &  $E_{\tau_3}$ ) (eV) for PMMA/ COMA blend filled with different concentrations of  $\text{CaCO}_3$ . -■- before Tg -●- after Tg.

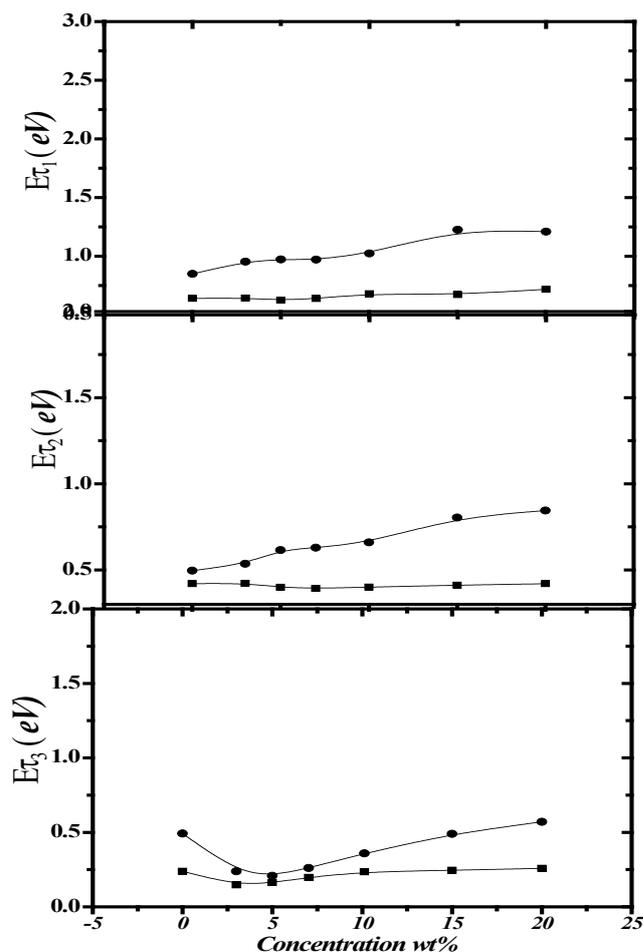


Fig. 12. Activation energies ( $E_{\tau_1}$ ,  $E_{\tau_2}$  &  $E_{\tau_3}$ ) (eV) for PMMA/COMA blend filled with different concentrations of nano  $\text{CaCO}_3$  -■- before Tg - ●- after Tg.

#### Electrical conductivity ( $\sigma_{dc}$ )

The electrical conductivity  $\sigma_{dc}$  for the investigated systems were calculated, and the data obtained for both fillers are shown graphically in Figure (13). It is evident that  $\sigma_{dc}$  increases with increasing temperature due to the raise of mobility of ionic bodies that occur as a result of excitation by heating. Furthermore, these figures indicate that a considerable increase in the values of  $\sigma$  up to concentrations 30 to and 10 wt% for both fillers, after which a steady increase is noticed. This could be attributed to the stability in the ionic motion expected to be achieved at those concentrations (network formation). This finding is supported by the investigation which was carried out using SEM given in Fig. 3 and 4.

The activation energy  $E_{\sigma}$  for the investigated systems were also determined according to Arrhenius equation. The data obtained for  $\sigma$  in case of both investigated fillers are plotted

graphically versus  $1000/T$ . The presence of knicks on the linear dependence of the Arrhenius plot indicates that two activation energies are detected below and above the glass transition temperature  $\sim 60$  °C.[18]. The data obtained for both energies  $E_{\sigma_1}$  and  $E_{\sigma_2}$  are illustrated graphically in Fig. 14 [19]. The higher values of  $E_{\sigma_2}$  incomparable with those of  $E_{\sigma_1}$  is considered to be an evidence for the change in the transport mechanism in the temperature region of glass transition.

From Fig. 13, it is interesting to find that the electrical conductivity  $\sigma_{dc}$  of PMMA/COMA blend can be used for antistatic applications up to concentrations 30 and 10 wt%  $\text{CaCO}_3$  in the micro and nano scales and at temperature not exceed  $60$  °C. On the other hand, when the concentration of  $\text{CaCO}_3$  exceeds 30 and 10 wt% and the temperature more than  $60$  °C, the blend is recommended to be used for electrostatic dissipation applications [16].

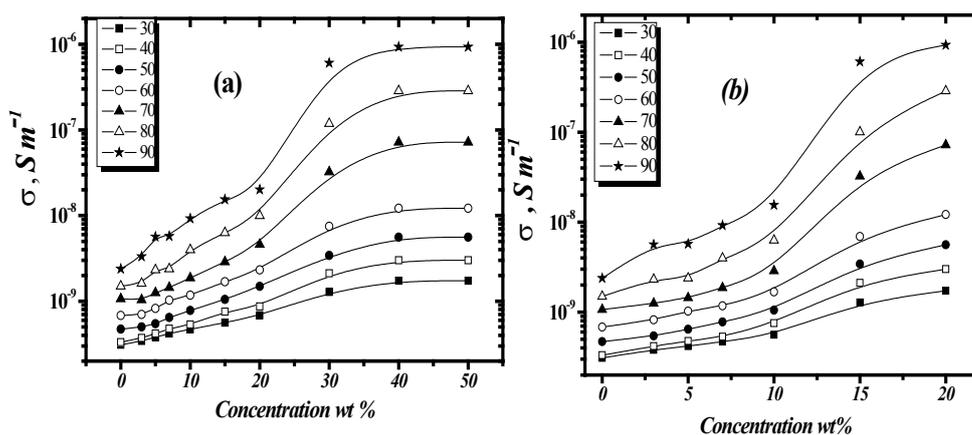


Fig. 13. Dependence of electrical conductivity ( $\sigma_{dc}$ ) ( $\text{Sm}^{-1}$ ) for PMMA/ COMA blend filled with  $\text{CaCO}_3$  (a) micro and (b) nano on concentration wt% at different temperatures  $^{\circ}\text{C}$ .

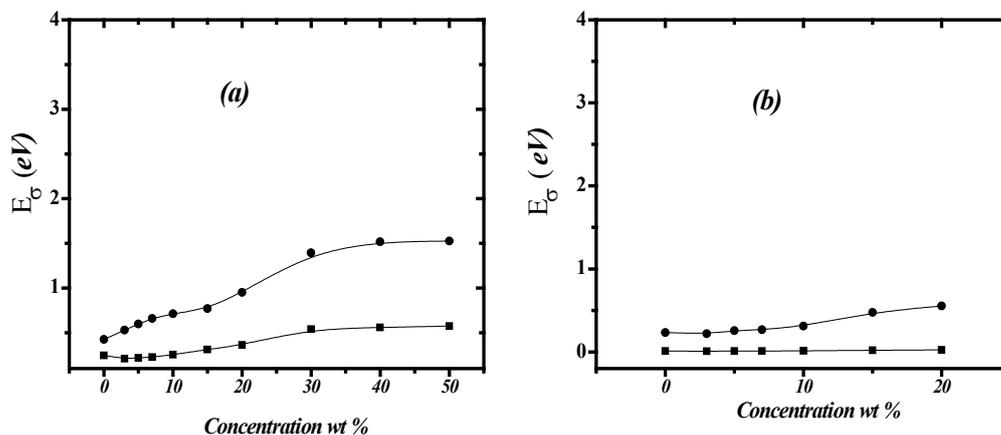


Fig. 14. Activation energy  $E_g$  (eV) for PMMA/ COMA blend filled with different concentrations of  $\text{CaCO}_3$  (a) micro and (b) nano -■- before Tg -●- after Tg.

#### Biodegradation

The effect of different concentrations of  $\text{CaCO}_3$  in micro and nano scales (0, 5, 15 and 40 wt%) for micro-sized and (0, 5 and 15 wt%) for the nano-sized on the enzymatic degradation of PMMA/COMA blend is studied. The composites were immersed in phosphate buffer solution up to 7 days. The obtained data are presented in Fig. 15a and 15b where the weight remaining is plotted against the time of immersion. As can be seen, the weight remaining decreases as time of immersion increases.

For PMMA/COMA 5 wt% of both filler sizes, the biodegradability decreased. This is may be due to the better dispersion of the filler in the matrix and a more tortuous path formed

for microorganism penetration inside the bulk hindered their diffusion. In addition, the degradation of the PMMA/COMA with nano-sized  $\text{CaCO}_3$  proceeds in higher rate than that of in the micro-sized  $\text{CaCO}_3$ . This is because the small particle size can lead to  $\text{CaCO}_3$  more easily distributed into PMMA/COMA blend than other one leading to higher solubility. From the same figures, it can be also seen that the fillers content practically influence  $\Delta\text{wt}$  values of the blend. where, the biodegradability increased by increasing filler content. This behavior could be explained on the basis of the tendency of filler particles to agglomerate and forming clusters in various shapes and sizes [20] and [21]. This in turn gives rise to strong filler-filler interactions together with bad dispersion in the matrix.

Through these clusters, which represent weak points in the matrix, water will be able to diffuse and weakens any possible bond between the filler and the polymer and may in some cases cause complete debonding due to hydrolysis, and the composites may be broken down by the enzymes secreted by microorganisms, in this case the

polymer is strongly degraded [22]. These results are supported by earlier studies, as it was observed that addition of layered silicate and calcium carbonate increased the rate of biodegradation of PLA [23] and [24]. Besides, the degradation rate of PLA in compost was delayed with the introduction of crosslinks [25].

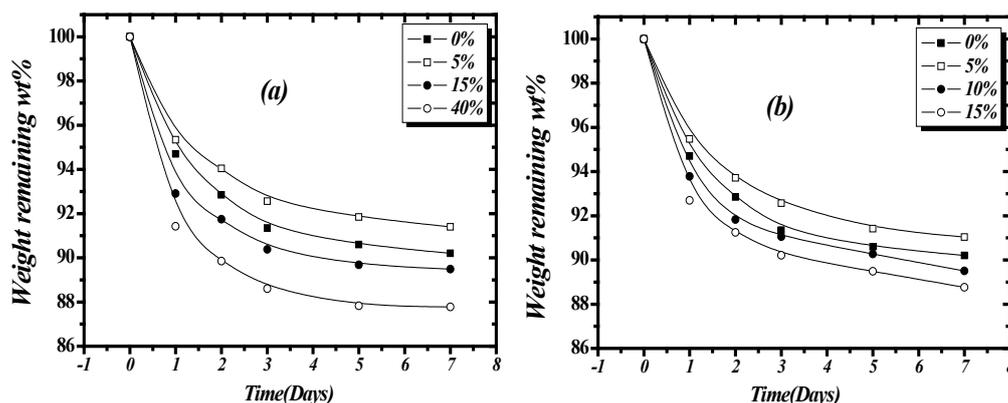


Fig. 15. Weight remaining (wt%) versus time (days) for PMMA/ COMA blend filled with different concentrations of CaCO<sub>3</sub> (a) micro (b) nano CaCO<sub>3</sub> at room temperature ~30 °C.

## Conclusion

The negative impact of synthetic polymers on the natural environment creates a lot of problems with deposition of waste and consumption. The main advantage of biodegradable polymers is not only reduce threats to wildlife caused by dumping conventional plastic but will also reduce the cost of labor for removal of plastic waste in the environment. In this research, the incorporation of the filler in the polymer matrix exhibits remarkable improvement in its properties. The two concentrations (10 and 30 wt%) were found to be the critical concentrations in case of the micro and nano CaCO<sub>3</sub> respectively. The composite films could be used for antistatic applications only below both the glass transition temperature and the critical concentrations while above these values, both blends could be used in electrostatic dissipation applications. Results of the biodegradation studies revealed that, all the blend films are degraded enzymatically. The biodegradation increase with increasing either the time of immersing or the filler concentration. The easiest dispersion of the nano filler in the polymer matrix show less biodegradability. These biodegradable composites can be recycled to useful monomers and oligomers by microbial and

enzyme treatments, so using these biodegradable polymers in a variety of industries instead of synthetic materials can significantly help to protect the natural environment.

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## الخواص البيوفيزيائية للبولي استرات التي تعتمد في تحضيرها على بعض الزيوت النباتية

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في هذا البحث تم اختيار البولي ميثاكريلات (PMMA) لعمل توليفات بنسب مختلفة مع COMA للحصول على خواص مبتكرة بالإضافة لإستخدامها في أغراض العزل الكهربى والتطبيقات الحيوية. وقد وُجِدَ أن كلا من ثابت العزل  $\epsilon$ ، و الفقد العزلى  $\epsilon$ » يزدادان بزيادة النسبة المئوية لكل من COMA بالتوليفة.

شارت نتائج التوصيلية الكهربائية  $\sigma_{dc}$  للمواد قيد الدراسة بإمكانية استخدام تلك التوليفات في تطبيقات الكهربائية الساكنة (antistatic applications). علاوة على ذلك، لوحظ أنّ العلاقة التي تربط التوصيلية الكهربائية  $\sigma_{dc}$  بتركيب التوليفات بأنها علاقة خطية وذلك حتى تركيز 30/70. هذا يُمكن أن يعزى إلى قابلية الاختلاط (miscibility) للتوليفات الموجودة فقط في هذا المدى. هذه النتيجة مدعومة من قبل نتائج دراسات أسطح التوليفات بالميكروسكوب الالكترونى الماسح SEM.

إندماج المادة المألثة في المصفوفة البوليمرية يؤدي الى حدوث تحسن ملحوظ بخواصها. وهذا ما تم التوصل إليه عند اضافة كربونات الكالسيوم ( $CaCO_3$ ) الدقيقة والنانومترية بنسب مختلفة الى التوليفة PMMA/COM. تم دراسة الأفلام المُحضّرة من تلك المتراكبات من خلال تقنيات مختلفة مثل: التحليل الحرارى TGA، الميكروسكوب الالكترونى الماسح SEM، المسح الحرارى التفاضلى DSC بالإضافة إلى الخواص العزلية وقد أوضحت النتائج حدوث زيادة في كل من ثابت العزل  $\epsilon$ ، و الفقد العزلى  $\epsilon$ » بزيادة كل من تركيز المادة المألثة ودرجة الحرارة.

كما أدت الدراسة التوصيلية الكهربائية  $\sigma_{dc}$  الى أنه يمكن استخدام هذه التوليفات كمضادات للشحنات الكهرواستاتيكية لكل من PMMA/COMA عند تركيزات أقل من 30% و 10% للمادتين المألثتين و درجة حرارة لا تزيد عن 60 C°، بينما عند التركيزات أكبر ودرجات حرارة أعلى فإنه قد أوصى باستخدامها في تطبيقات تبديد الكهرباء الساكنة

اضافة لذلك فقد تم دراسة تأثير التركيزات المختلفة لكربونات الكالسيوم ( $CaCO_3$ ) الدقيقة والنانومترية على التحلل الانزيمى لهذه المتراكبات ووجد أن الوزن المتبقى قد نقص بزيادة إما زمن الغمر أو تركيز المادة المألثة. هذا وقد نوقشت النتائج على اساس حدوث تكثف وتجمع للمادة المألثة والذى من المتوقع حدوثه خصوصا بزيادة محتوى المادة المألثة. وهذه النتيجة قد دعمت بنتائج الميكروسكوب الالكترونى الماسح (SEM). بصفة عامة فإن سهولة توزيع جزيئات كربونات الكالسيوم ( $CaCO_3$ ) النانومترية في المصفوفة هو المسئول عن النقصان في التحلل البيولوجى (الطبيعى).