

The Effect of Modified Pluronic on the Distribution of Fillers in the Polyvinyl Chloride Matrix

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Received 14 December 2008; accepted 2 August 2009

DOI 10.1002/app.31217

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Pluronic was modified by using maleic anhydride (MA) and was characterized by means of FTIR and ¹H NMR. Polyvinyl chloride (PVC) was blended with different contents of modified pluronic (MPL). After 20% by weight MPL, no significant change was noticed in either the electrical or the mechanical properties. The addition of 10 wt % MPL to PVC loaded with different contents of titanium oxide (TiO₂) and sodium bentonite was chosen to act as a dispersing agent for the two types of fillers. This result was obtained through the measurements of permittivity ϵ' and dielectric loss ϵ'' at the frequency range (10²–10⁵ Hz) in addition to the electrical conductivity (σ). According to Arrhenius equation, the activation related to both conductivity E_{σ} and relaxation

time E_{τ} in addition to the experimental σ_0 were found to confirm the validity of compensation law for the semiconducting PVC system. The increase of ϵ' and ϵ'' by increasing filler content in the presence of 10% MPL in comparison with those before the addition of such concentration of MPL indicates a homogenous distribution of filler in the PVC matrix. This result finds further justification through the mechanical measurements and the scanning electron micrographs. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1732–1741, 2010

Key words: polyvinyl chloride; modified pluronic; electrical; mechanical properties; scanning electron microscope

INTRODUCTION

The dielectric properties of polymers have been of great interest to many workers. The close relation between the mechanical properties warrants such interest, in addition to the direct application to the problem of electrical insulation.¹

The nature of relaxation processes of polymer blends is a powerful tool for the study of molecular motions and manner in which they are affected by different factors.^{2,3}

In general, the dielectric properties of polymers and polymer blends depend on structure, crystallinity, morphology, and the presence of other additives.

The water-soluble triblock copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO), commercially known as pluronic has found many industrial applications as emulsifying, wetting, thickening, coating, solubilizing, stabilizing, dispersing, lubricating, and foaming agents. This could be attributed to their importance in practical applications as detergents, emulsifiers,

defoaming agents, dispersants, or vehicles in pharmaceutical formulations.^{4–7}

In recent years, modifications of PEO–PPO–PEO block copolymers are being explored for various applications.^{8–11}

The modification of pluronic with maleic anhydride is a new biocompatible copolymer based on grafting maleic anhydride onto the pluronic backbone by means of a catalyst. The modification of pluronic leads to a change in the ratio of hydrophilic–lipophilic properties that meet the specific requirements in different applications, such as interaction with a wider range of additives.

Polyvinyl chloride (PVC) is one of the major thermoplastics used today.¹² However, because of its inherent disadvantages, such as low-thermal stability and brittleness, PVC and its composites are subject to some limitations in certain applications.¹³ Preparing PVC composites may be one of the effective ways to improve this material's performance.

Fillers have an important role in modifying the properties of various polymers and lowering the cost of their composites. The effect of the fillers on the composites properties depends on their concentration, their shape and particle size, aggregate size, surface characteristics, and degree of dispersion. It has been reported that the degree of dispersion of the fillers in a polymer matrix has significant effects on the mechanical properties of these

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composites.^{14,15} The homogeneous dispersion of fillers in the polymeric matrix is mostly difficult because of their tendency to agglomerate.

The aim of this work is to investigate the electrical and the mechanical properties of PVC/ modified pluronic (MPL) blends of different concentrations. Also, to study the role of the addition of MPL as dispersing agent to the PVC filled with two different types of fillers (TiO₂ and sodium bentonite) and study the various properties before and after such addition.

EXPERIMENTAL

Materials

Pluronic 3100 poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) was from BASF with molecular weight 1000 g/mol, maleic anhydride (MA), and *p*-toluene sulphonic (PTSA used as a catalyst) were supplied by Merck-Schuchardt (Germany). The general-purpose polyvinyl chloride (PVC) resin used was a white powder made by suspension polymerization with *k* value of 67 from El-Amerria (Alexandria, Egypt). The fine grade of titanium oxide (TiO₂) (with particle size 467 nm) was supplied by HOMBITAN FF. pharma Sachtleben Chemx GMBH Germany. Sodium bentonite clay was obtained from BASF Germany (with particle size 870 nm).

Synthesis of modified pluronic (MPL)

Pluronic was carboxylated with maleic anhydride (MA) to produce monocarboxy pluronic (MPL). The synthesis of the modified Pluronic (MPL) was performed as follow: 2.94 g maleic anhydride (1 mol) and 30 g of pluronic (1 mol) were placed into the reactor in an oil bath at 180°C under vacuum in the presence of 0.0294 g PTSA (1 wt % based on maleic anhydride) as a catalyst for two hours to perform the melt-polycondensation reaction.

Preparation of PVC/MPL blends by solution casting technique

The required solutions were prepared by dissolving 5 g of each PVC and MPL separately in 100 mL chloroform. Films of polymer blends (PVC/MPL) were prepared by casting the mixed solution of different ratios (0/100, 5/95, 10/90, 20/80, 30/70, 40/60, and 50/50 wt %) on a glass plate with slow drying at room temperature. Care was taken to control the uniform thickness of the film for all compositions. Clear films were obtained. The micrometer was used to measure film thickness which was found to be in ranging from 0.10 to 0.15 mm.

Preparation of PVC composites

PVC composites were prepared by mixing different ratios of each filler of titanium oxide (TiO₂) and sodium bentonite (0–8 %) with PVC solution (5 wt % in THF) with and without 10 wt % MPL as a dispersing agent and sonicated for 5 min. Films were prepared from the dispersions using the conditions provider above. The film thickness was controlled by using the same solution concentration of the polymers under investigation.

Instrumental analysis

FTIR spectroscopy (JASCO type 300E, Japan) and ¹H NMR spectroscopy (JEOL type EX 270 MH, Japan) were used.

The mechanical properties of the films obtained were determined with a Zwick 1425 tensile tester at 25 °C and at a crosshead speed of 500 mm/min according to ASTM D 412-98a.

A scanning electron microscope (SEM), JXA- 840A JEOL (Japan), with an applied voltage 20 kV was used. SEM was performed on surface of particle samples after coated with a thin layer of gold to assure electron conductivity between the samples and the specimen stage.

Dielectric measurements were performed in the frequency range of 100 Hz–100 kHz by using an LCR meter type AG-411 B (Ando electric Ltd., Japan). The capacitance *C*, the loss tangent $\tan \delta$, and the resistance *R* were obtained directly from the bridge from which the permittivity ϵ' , dielectric loss ϵ'' , and conductivity σ were calculated. A guard ring capacitor type NFM/5T Wiss Tech. Werkstätten (WTW) GMBH Germany was used as a measuring cell. The cell was calibrated by using standard materials¹⁶ and the experimental error in ϵ' and ϵ'' was found to be $\pm 3\%$ and $\pm 5\%$, respectively. The temperature was controlled using an ultrathermostat. The experimental error in temperature controlling was 0.1°C.

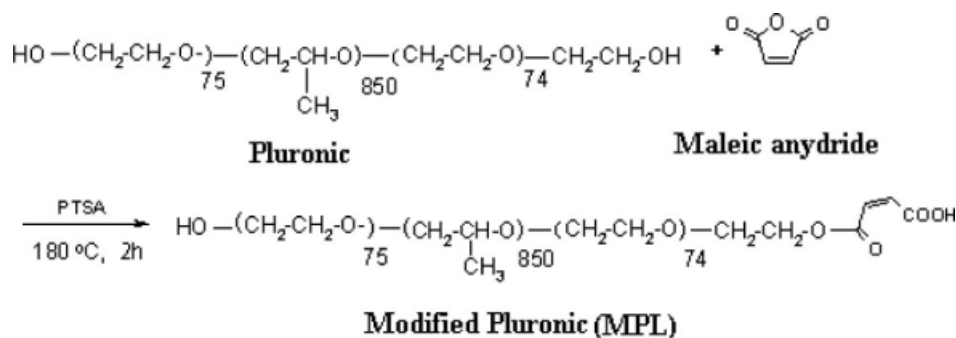
RESULTS AND DISCUSSION

Characterization of modified pluronic

Modified pluronic with maleic anhydride (MPL) was prepared according to the following scheme:

The chemical structure of the MPL was characterized by means of FTIR and ¹H NMR spectroscopy.

The FTIR spectra of pluronic and MPL are shown in Figure 1. The spectrum of MPL shows peaks at 1637 and 1274 cm⁻¹, namely the vibration absorbing peaks of –CH=CH– group of maleic anhydride. Moreover, strong vibration absorption peak of carbonyl group C=O exists at 1740 cm⁻¹ in the corresponding curve.



Scheme 1 Synthesis of modified pluronic (MPL).

^1H NMR data confirmed the chemical composition of the modified pluronic (MPL) (Fig. 2). The signals at 6.5–6.7 ppm, characteristic of the (olefinic proton) $-\text{CH}=\text{CH}-$ in the maleic acid residue, indicate the modification of the pluronic with maleic anhydride. However, introducing pluronic into the anhydride would cause small shift for methyl protons of pluronic block ($\text{O}-\text{CH}_2-\text{CH}_2$) and ($\text{OCH}_2\text{CH}(\text{CH}_3)$) at $\delta = 3.65$ ppm.

Electrical properties of PVC/ MPL blends

Figure 3 displays plots of the permittivity ϵ' and dielectric loss ϵ'' vs. frequency for the PVC blended with various content of MPL at 30°C . It can be seen that the permittivity ϵ' of the composites varies from 4.4 to 12 as the MPL concentration increased to 50 wt % at 100 Hz as shown in Figure 4.

The increase in ϵ' is more pronounced until 20 wt % after which a slight increase was noticed. Moreover, it is found that ϵ' drastically decreases with increasing frequency showing anomalous dispersion. To discuss the relaxation mechanisms associated with such dispersion, the dielectric loss values ϵ'' are plotted graphically vs. the applied frequency, f , as

shown in Figure 3. From this figure, it is clear that the values of ϵ'' increase from 0.1 to 0.63 by increasing the (MPL) content as shown in Figure 4. Also, it is clear that the values of ϵ'' are broad indicating more than one relaxation mechanism is expected. As it is known, the main contributions to the ϵ'' values of the composites are two polarizing processes. The first is an interfacial polarization, which was induced through a local accumulation of free charges captured by defects or interfaces in the composites, and it relaxed at about 5×10^2 Hz because of Maxwell Wagner effect. The second process attributed to the polarization of various sized dipoles. Analysis of the absorption curves relating ϵ'' and the applied frequency after subtracting the conductivity part was done in terms of superposition of one Fröhlich and a Havriliak–Negami functions according to the equations given before.¹⁷

The first absorption region lies in the lower frequency range found to be about $2.8\text{--}3.2 \times 10^{-4}$ s, which is attributed to Maxwell Wagner effect always appears in such range of frequency because of the multiconstituents of the sample. This region is found to be unaffected by the MPL content. The second absorption region with relaxation time τ_2 in the order of 10^{-5} s, which is fitted by Havriliak–Nagami function with $\alpha = 0.3$ and $\beta = 0.7$. This region with

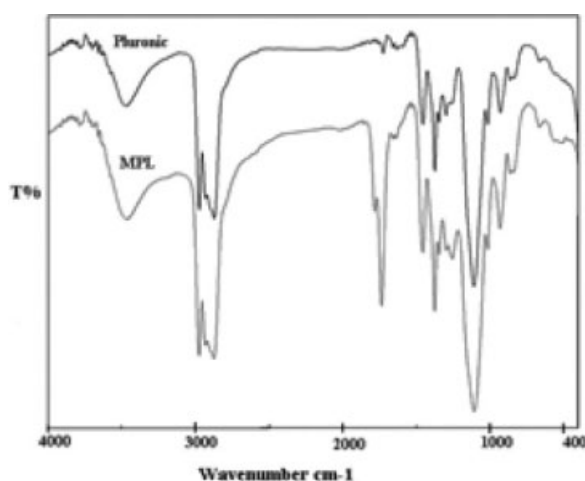


Figure 1 IR spectra of the pluronic and the modified pluronic (MPL).

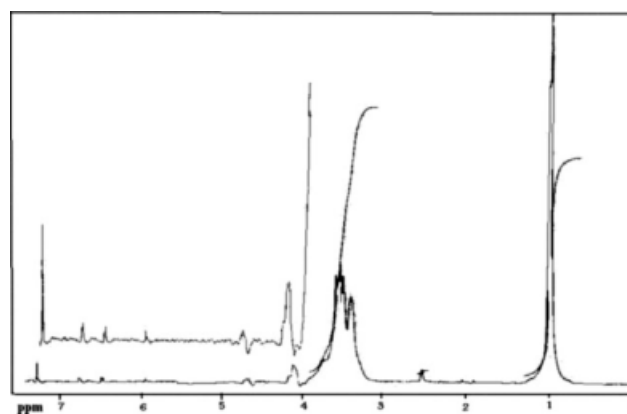


Figure 2 ^1H NMR of the MPL.

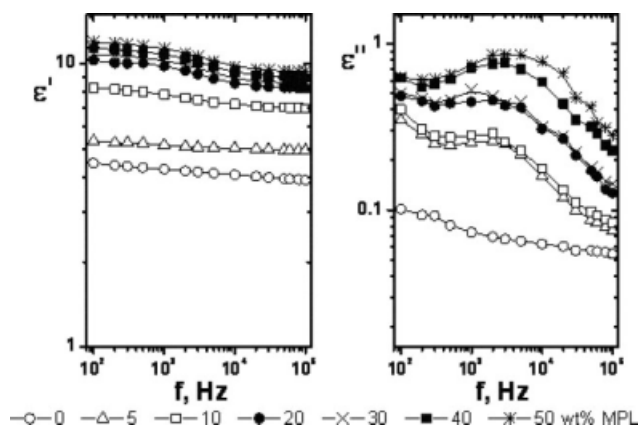


Figure 3 Permittivity ϵ' and dielectric loss ϵ'' vs. applied frequency for PVC with various MPL content at 30°C.

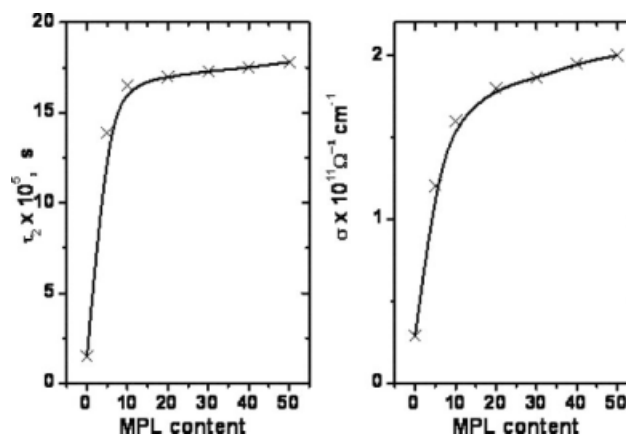


Figure 5 Variation of the second relaxation time τ_2 and the electrical conductivity σ vs. MPL content.

relaxation time τ_2 could be associated with some local molecular motions rather than the main chain motion as it is frozen because the measurements were performed at 30°C, i.e., lower than the T_g .¹⁸

Figure 5 represents the variation of both τ_2 and the electrical conductivity σ vs. MPL content. From this figure, it is clear that the relaxation time τ_2 which ascribe this region is found to increase by increasing MPL content until 20 wt % after which no significant change is noticed. This increase may be due to some sort of physical interaction between MPL molecule and PVC matrix. This interaction could increase the molar volume of the rotating units and consequently the relaxation time. From the same figure, it is also clear that the electrical conductivity σ follow the same trend of τ_2 .

Example of the analyses is given in Figure 6 for PVC free from MPL and that contains 20 wt % MPL.

From the above investigation, it is concluded that no significant change in electrical properties is noticed by increasing MPL until concentration 20 wt %. For such reason, the permittivity ϵ' and

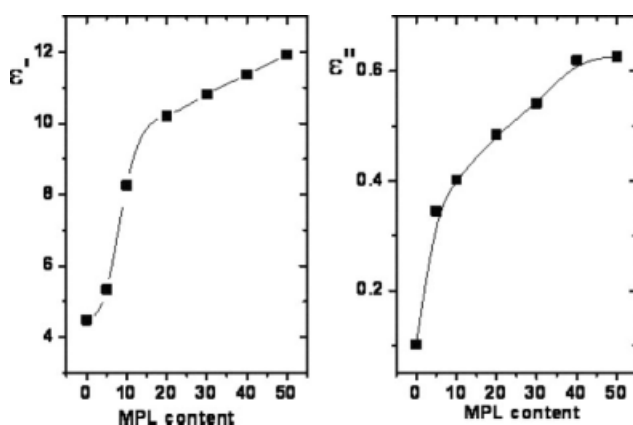


Figure 4 Permittivity ϵ' and dielectric loss ϵ'' vs. MPL content at $f = 100$ Hz at 30°C.

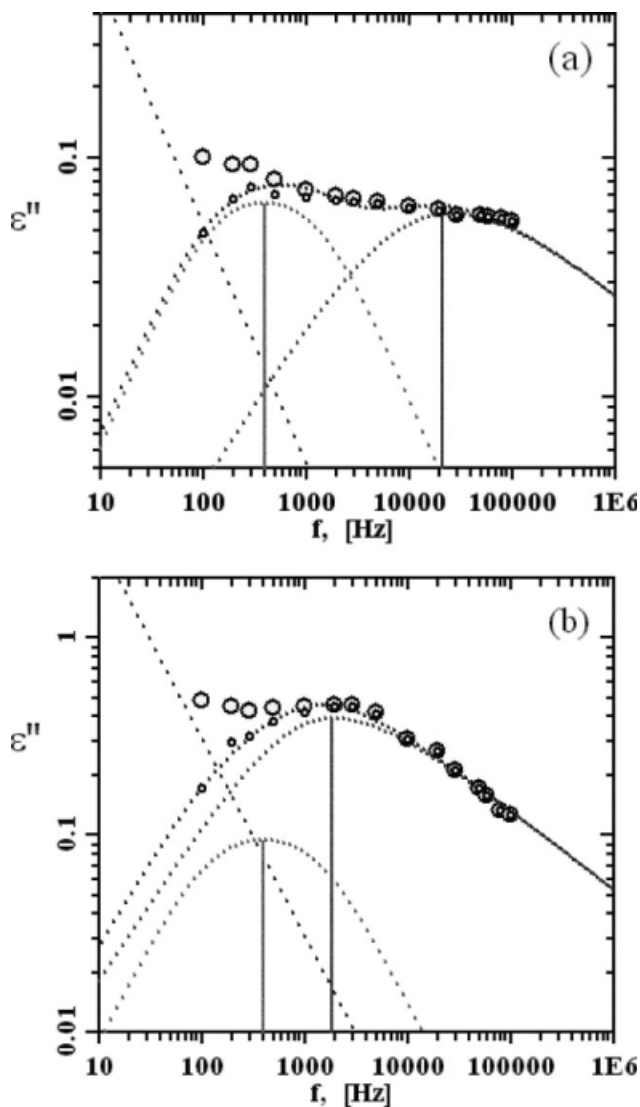


Figure 6 Example of the analyses for (a) PVC and (b) PVC + 20 wt % MPL. The experimental data were fit after the subtraction of the losses because of direct-current conductivity with Fröhlich and Havriliak-Negami functions.

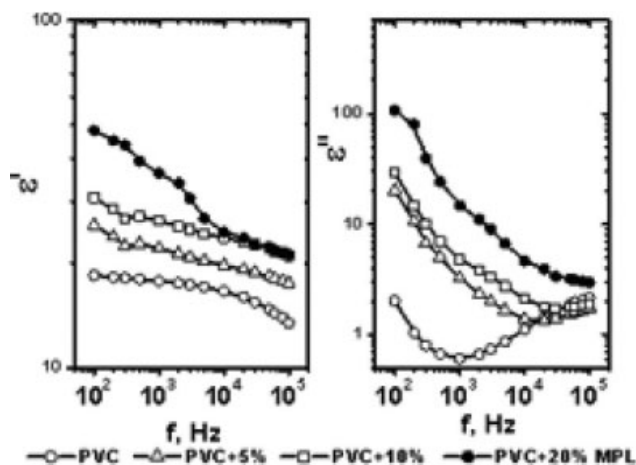


Figure 7 Permittivity ϵ' and dielectric loss ϵ'' vs. applied frequency for PVC with various MPL content at 90°C.

dielectric loss ϵ'' were performed at different temperatures ranging from 30 to 98°C, which cover the temperature range of the glass transition of PVC with the different concentrations up to 20 wt % MPL.

Example of these measurements is illustrated graphically in Figure 7 for the blend under investigation at 90°C.

Comparing Figures 3 and 7, one can see that there is a dramatic change in both ϵ' and ϵ'' as both values are higher at 90°C, when compared with those at 30°C. On the other hand, the shape of the curves relating ϵ'' and the applied frequency are changed due to the dramatic increase in the electrical conductivity and the shift of the second relaxation process toward the higher frequency. Figure 8 illustrates the effect of temperature on ϵ' and ϵ'' for the different content of MPL at fixed frequency (100 Hz). From this figure, it is clear that both values increase by increasing MPL content or temperature. An abrupt increase in both values occurs after 70°C this near the glass transition temperature $\approx 87^\circ\text{C}$.¹⁹

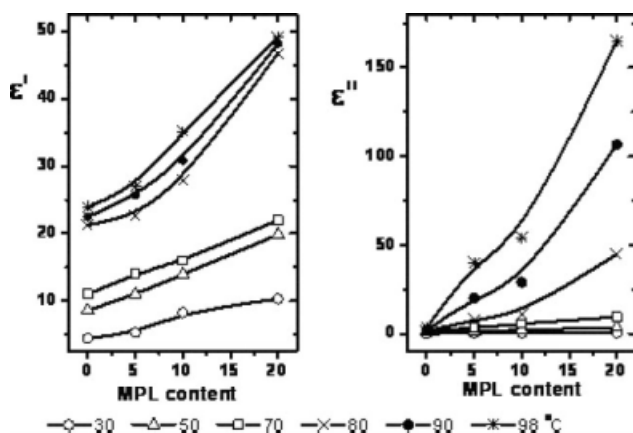


Figure 8 Permittivity ϵ' and dielectric loss ϵ'' vs. MPL content at $f = 100$ Hz and at different temperatures.

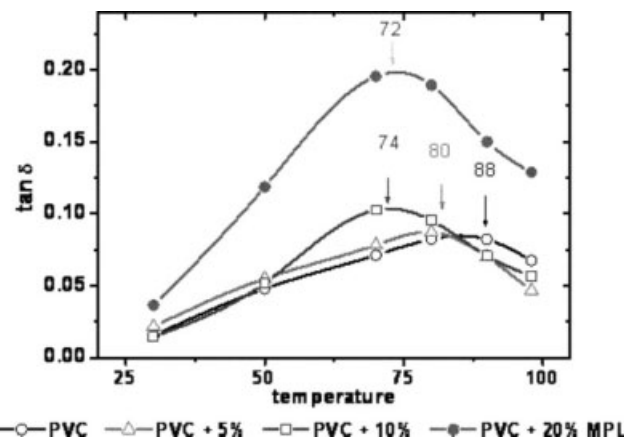


Figure 9 Relation of $\tan \delta$ at $f = 100$ kHz and temperature for PVC with various content of MPL.

To confirm this assumption, the relation between $\tan \delta$ and temperature was illustrated graphically in Figure 9 to show how the glass transition temperature is affected by the increasing MPL content.

From this figure, it is clear that the glass transition temperature T_g of PVC at 88°C is comparable with that obtained in literature.¹⁹ Also it is clear that T_g decreases from 88 to 72°C by increasing MPL content. This decrease is attributed to the physical interaction between the MPL molecule and the PVC matrix, which was the reason for increasing the relaxation time τ_2 as mentioned earlier.

The curves relating ϵ'' and the applied frequency were analyzed in the same way mentioned earlier. After subtraction of the losses due to dc conductivity, the data reveal two relaxation processes. The first absorption region lies in the lower frequency range and fitted by Fröhlich function found to be about $2.8\text{--}3.2 \times 10^{-4}$ s may be attributed to Maxwell Wagner effect, which always appear in such range of frequency because of the multiconstituents of the

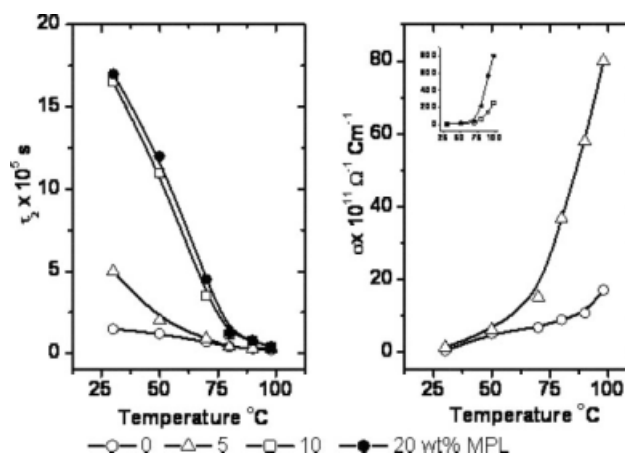


Figure 10 Variation of relaxation time τ_2 and the electrical conductivity σ vs. temperature.

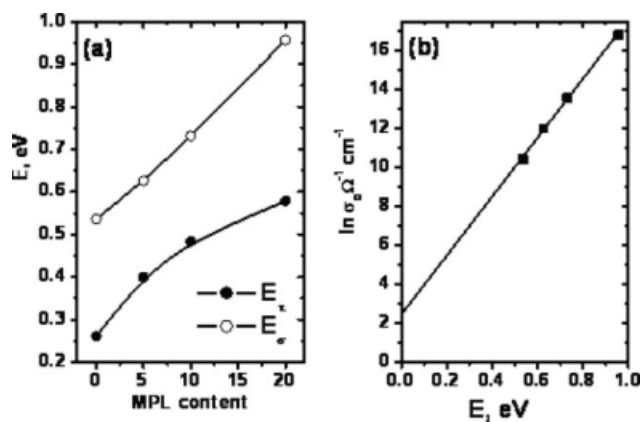


Figure 11 Relation between (a) activation energy E and MPL content and (b) σ_0 and activation energy E .

sample. This region is found to be unaffected by either the MPL content or the temperature. The second absorption region with relaxation time τ_2 in the order of 10^{-5} s, which is fitted by Havriliak-Nagami function with $\alpha = 0.3$ and $\beta = 0.7$. At temperature below the glass transition temperature, this region with relaxation time τ_2 could be associated with some local molecular motions rather than the main chain motion as it is frozen. At temperatures higher than T_g , this process could be attributed to the combination of the large scale mobilization of the chains, i.e., the glass rubber relaxation process in addition to a contribution of the motion of the large aggregates caused by the movement of the main chain, which are expected to be formed by the addition of different ingredients to PVC such as plasticizer,²⁰ etc. The obtained relaxation time τ_2 associated with this region was illustrated graphically in Figure 10 together with the dc conductivity σ . From this figure, it is clear that the second relaxation process decreases by increasing temperature. This decrease is due to the increase in the mobility. The electrical conductivity σ is found to increase by increasing the temperature showing positive temperature coefficient on the base of such behavior one can see that these blend behave like semiconductor materials although the values of σ does not exceed $10^{-9} \Omega^{-1} \text{cm}^{-1}$. This finding recommends this blend to be used as antistatic materials as its electrical conductivity lies in the order of $10^{-9} - 10^{-14} \Omega^{-1} \text{cm}^{-1}$, which is the range recommended for such purposes.

The increase of the electrical conductivity by increasing temperature is determined by thermally assisted hopping or, possibly, charge tunneling between the conducting particles. The temperature dependence of conductivity σ can be expressed by an Arrhenius equation

$$\sigma = \sigma_0 \exp(-E/kT)$$

where E is the activation energy of conductivity, k is the Boltzmann constant, T is the temperature, and σ_0 is a preexponential factor depending on mobility of charge carriers. Same relation can be used to calculate the activation energy accompanied by the second relaxation process by replacing σ and σ_0 by τ_2 and τ_0 .

The experimental data for various semiconducting materials showed that correlation between $\ln \sigma_0$ and E is linear:

$$\ln \sigma_0 = a + bE$$

where constants a and b are >0 . This relation is called as the Meyer-Neldel rule²¹ or the "compensation law"²² was first described for inorganic oxides. However, later on, its general validity for various kinds of semiconducting materials, inorganic or organic, has been demonstrated.²³

For all the investigated composites $\ln \sigma$ was plotted vs. $1/T$, straight lines were obtained from which the activation energy E and σ_0 were obtained. Figure 11 represent the variation of the activation energy obtained for both the conductivity σ and the relaxation time τ_2 and the dependence of $\ln \sigma_0$ on E . From this figure, it is clear that both values increase by increasing MPL content and the dependence of $\ln \sigma_0$ on E is linear, this confirm the validity of the compensation law for the blend system.²⁴

Mechanical properties of PVC/MPL blends

PVC/MPL blend films were cut with a dumbbell-shaped cutter. Crosssection areas of the dumbbell specimens were measured accurately with the aid of a thickness gauge. The mechanical properties of the blend films with different blend were measured and are illustrated in Figure 12.

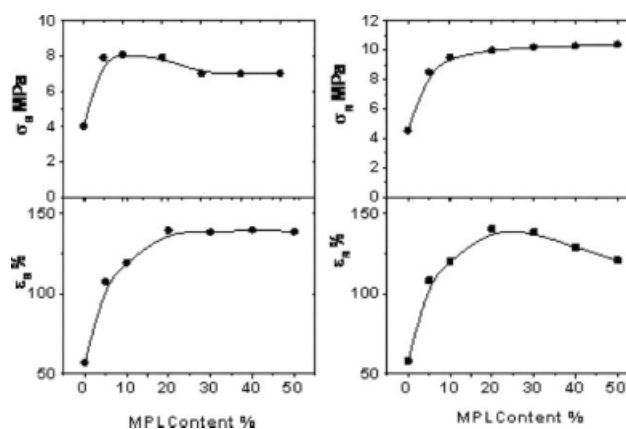


Figure 12 Relation between stress at yield σ_B , stress at rupture σ_R , strain at yield ϵ_B and strain at rupture ϵ_R vs. MPL content.

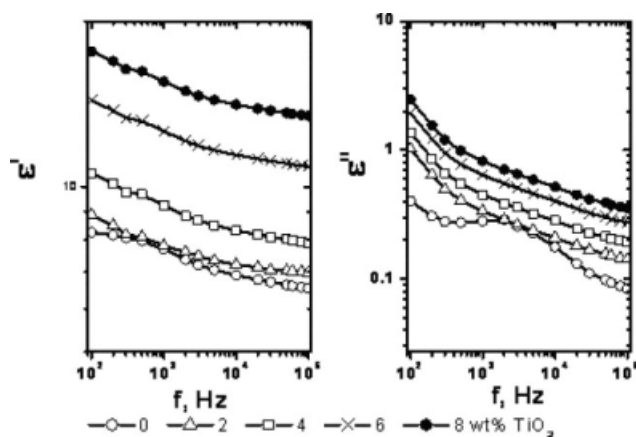


Figure 13 Permittivity ϵ' and dielectric loss ϵ'' vs. applied frequency for PVC+10% MPL loaded with TiO_2 at 30°C .

Figure 12 represents the variation of the mechanical properties (stress at yield, stress at rupture, strain at yield %, and strain at rupture %) vs. the MPL content in PVC/MPL blends. This figure cleared that all the mechanical properties pronouncedly increased by increasing MPL until 20 wt % after which this increase become very small. This means that the presence of MPL with concentration of 20 wt % is enough to improve the mechanical properties of PVC. This result agrees with that found before by the dielectric measurements.

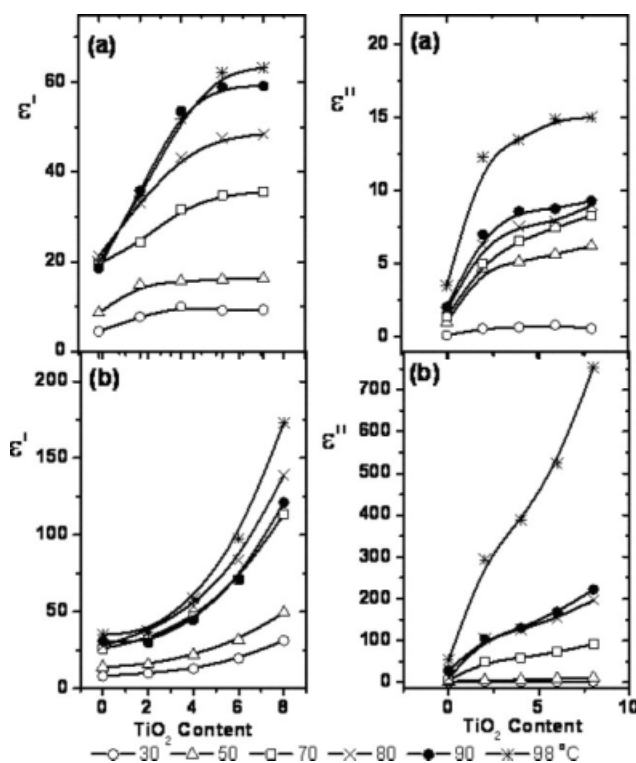


Figure 14 Variation of ϵ' and ϵ'' at 100 Hz vs. TiO_2 content (a) PVC and (b) PVC/10 wt % MPL.

From the above investigation, it could be concluded that the addition of MPL to PVC by a concentration more than 10 wt % does not affect its properties and for such reason this concentration was chosen to act as a dispersing agent for the two types of fillers (titanium oxide and sodium bentonite).

Electrical properties of PVC/MAL blends loaded with titanium oxide and sodium bentonite

The permittivity ϵ' and dielectric loss ϵ'' were measured over the frequency range 100 Hz and 100 kHz and at various temperature $30\text{--}98^\circ\text{C}$ for PVC loaded with TiO_2 and sodium bentonite with various concentrations from 0 to 8 wt % before and after the addition of 10 wt % MPL. Example of these measurements is illustrated graphically in Figure 13.

Figures 14 and 15 show the obtained data of the permittivity ϵ' and dielectric loss ϵ'' at $f = 100$ Hz at various temperatures ($30\text{--}98^\circ\text{C}$) before and after the addition of 10% MPL. Both ϵ' and ϵ'' are found to increase by increasing temperature. On the other hand, both ϵ' and ϵ'' values are found to increase slightly after 2 wt % filler before the addition of MPL, whereas these values increase pronouncedly by addition of 10 wt % MPL. This increase in both ϵ' and ϵ'' values indicates a homogenous distribution of the fillers in the PVC matrix in the presence of the 10 wt % MPL indicating role a dispersing agent.

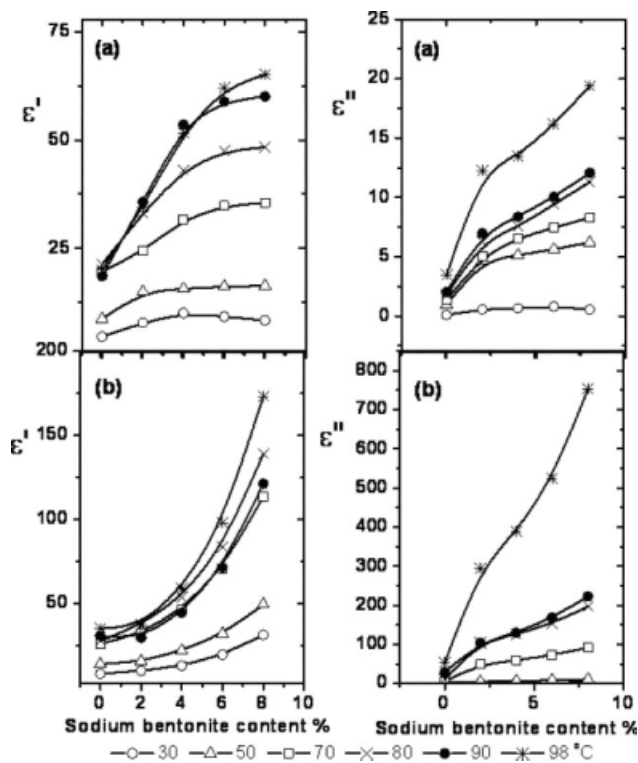


Figure 15 Variation of ϵ' and ϵ'' at 100 Hz vs. sodium bentonite content (a) PVC and (b) PVC/10 wt % MPL.

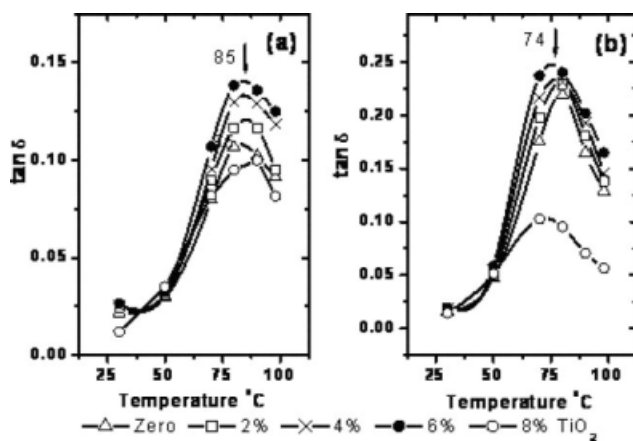


Figure 16 Tan δ vs. temperature for PVC loaded with different concentration of TiO_2 .

This preassumption find further justification through the scanning electron microscope and mechanical properties.

The variation of tan δ with temperature which reflect the variation in the glass transition temperature T_g were plotted graphically in Figures 16 and 17 for PVC loaded with TiO_2 and sodium bentonite, respectively, before and after the addition of the MPL. From these figures, it is seen that the glass transition temperatures (T_g s) are only affected by the presence of MPL as mentioned above not change by the addition of filler. This finding suggests that there is no interaction between the two fillers under investigation and the PVC matrix.²⁵

This finding achieves further justification through the second relaxation time τ_2 , which was found to be unchanged by increasing either filler content or its type. This finding suggests no change in the molar volume of the rotating units and consequently no interaction between the fillers and PVC matrix.

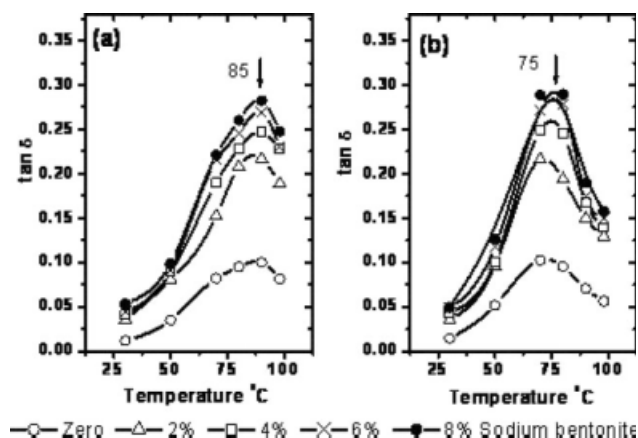


Figure 17 Tan δ vs. temperature for PVC loaded with different concentration of sodium bentonite.

Figure 18 represents the variation of the electrical conductivity σ vs. temperature for all the investigated samples.

From this figure, it is clear that the electrical conductivity of these composites increase by increasing temperature showing positive temperature coefficient. This increase is several times higher after the addition of the 10% MPL as a disperser agent. From the above figure, it can be concluded that these composites behave like semiconductor materials although the values of σ does not exceed $10^{-9} \Omega^{-1} \text{cm}^{-1}$. This finding recommends these composites to be used as antistatic materials as its electrical conductivity lies in the order of $10^{-9} - 10^{-14} \Omega^{-1} \text{cm}^{-1}$, which is the range recommended for such purposes.

Mechanical properties of PVC/MAL blends loaded with titanium oxide and sodium bentonite

Figures 19 and 20 represent the variation of the mechanical properties (stress at yield, stress at rupture, strain at yield %, and strain at rupture %) vs. filler content for PVC and PVC/10% MPL.

From these figures, it is clear that for PVC composites it is notable that the mechanical properties increase by the addition of 2% filler after, which the values of these mechanical parameters are slightly affected by the increasing of the concentration of the

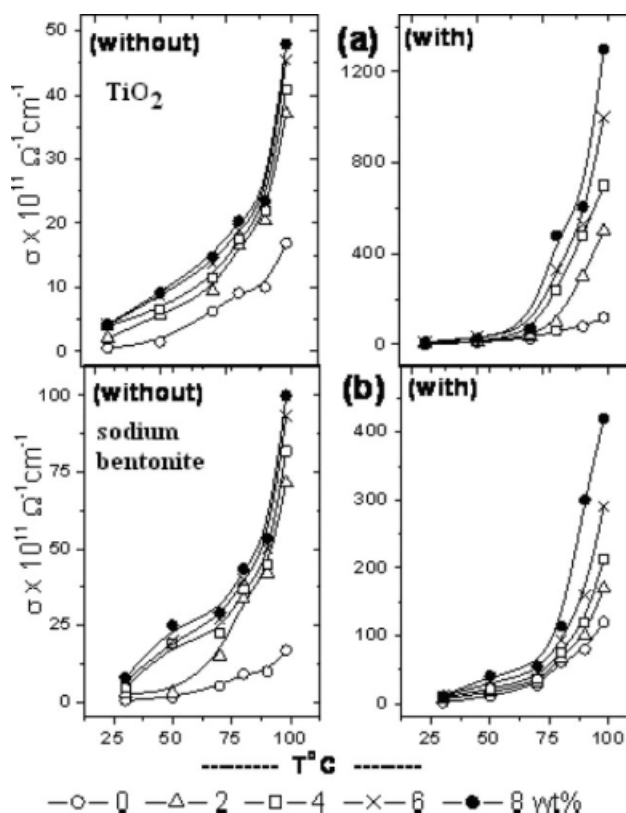


Figure 18 Variation of electrical conductivity σ vs. temperature for (a) TiO_2 and (b) sodium bentonite.

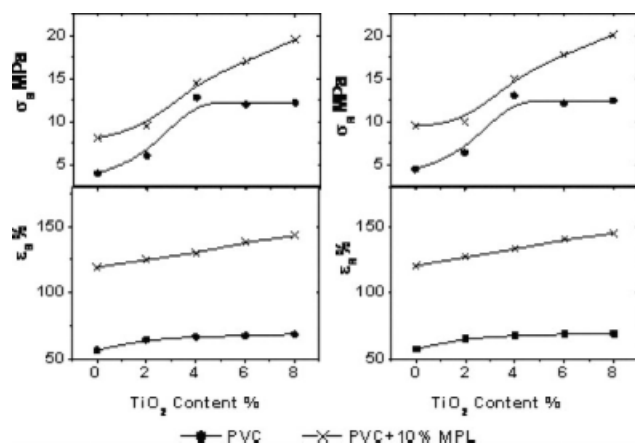


Figure 19 Relation between stress at yield σ_B , stress at rupture σ_R , strain at yield ϵ_B and strain at rupture ϵ_R vs. TiO_2 content.

fillers. This result may be due to the aggregation of the fillers in the PVC/ matrix which poor to some extent its properties. On the other hand, for PVC/ +10% MPL, all the mechanical properties are higher than PVC composites and increase by increasing filler content this enhancement in the mechanical properties is due to the fine distribution of fillers inside the PVC matrix. This finding support the results obtained by the dielectric measurements.

Morphological studies

Figure 21 represents the scanning micrograph for pure PVC and those for PVC loaded with 6 wt % of each filler as an example with and without 10% MPL. From this figure, it is clear that fine distribution of the fillers in the PVC matrix is occurred after the addition of 10% MPL, whereas the aggregation of the fillers is clear for samples without MPL. These micrographs support the presumption suggested from the dielectric measurement, which is that the addition of 10%

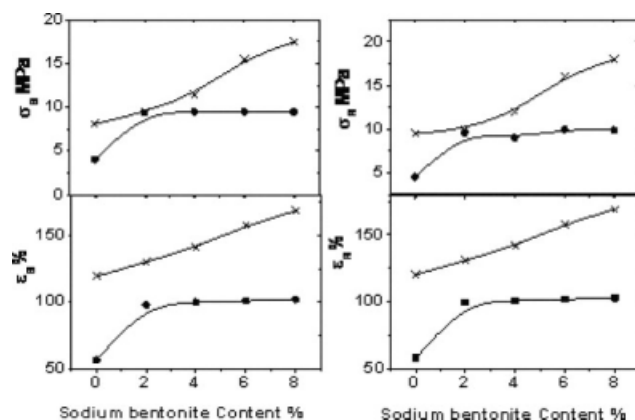


Figure 20 Relation between stress at yield σ_B , stress at rupture σ_R , strain at yield ϵ_B and strain at rupture ϵ_R vs. sodium bentonite content.

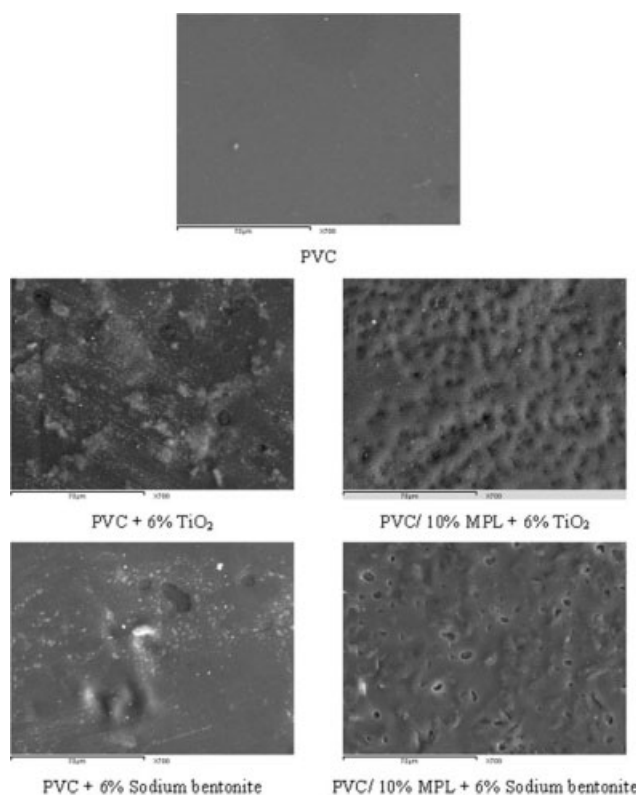


Figure 21 Scanning electron micrograph for PVC filled with TiO_2 and sodium bentonite before and after the addition of MPL.

help to some extent in solving the problem of aggregation of fillers inside the polymeric matrix.

The above investigation led to a conclusion that the addition of MPL with concentration 10% acts as a good dispersing agent for the PVC composites under investigation.

CONCLUSION

PVC was blended with different concentration of modified pluronic (MPL). The modification of pluronic was performed by maleic anhydride and investigated by FTIR and ^1H NMR spectroscopy. The dielectric and the mechanical properties of these blends was studied, and the data obtained indicated that no change in these properties at concentration of MPL higher than 20% by weight was detected. Such properties were also carried out with PVC loaded with different concentrations of TiO_2 and sodium bentonite before and after the addition of 10 wt % MPL as a dispersing agent. The addition MPL indicated a homogenous distribution of filler in the PVC matrix. This result was supported by the scanning electron microscopy investigation.

These investigations were carried out through the permittivity ϵ' , dielectric loss ϵ'' , and loss tangent $\tan \delta$ in addition to the electrical conductivity σ . The ϵ''

data were analyzed using Fröhlich and Havriliac–Nagami functions in which the relaxation time (τ_2) describing the mobility of the main chain and its related motions rather than the relaxation (τ_1) related to Maxwell Wagner effect were obtained. No significant change in τ_2 was found using both types of fillers before and after the addition of MPL indicating that no interaction was expected between the filler and polymer matrix. The activation energy E_σ and E_τ obtained using Arrhenius equation was found to confirm the validity of compensation law for the semiconducting PVC system.

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