나노 충전제의 분산을 정량화하기 위한 폴리에틸렌-클레이 나노 복합체의 유전특성 연구

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Investigation of Dielectric Properties of Polyethylene-Clay Nanocomposites for Quantifying Nanofiller Dispersion

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Abstract: This study examined the dielectric properties of linear low density polyethylene (LLDPE)/organo-clay nanocomposites including the same amount of maleic anhydride grafted polyethylene (PE-*g*-MA) and oxidized polyethylene (OxPE) as compatibilizer at different frequencies (10^{-1}-10^{+7} Hz) and temperatures (237-373 K). The dielectric constant of natural LLDPE remained constant at around 1.5, depending on the temperature rise and frequency while that of LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites increased up to 4.8 and 2.8, respectively, linearly with increasing temperature. Especially in the low frequency region, a Maxwell-Wagner-Sillars polarization was observed in composite structures with an increase in temperature due to the dipolar effect. It has been concluded that the clay in the polymer matrix was more homogeneously dispersed than OxPE due to the compatibilizing effect of PE-*g*-MA and that different polarization mechanisms were at play for each compatibilizer.

Keywords: low density polyethylene, composites, nanoparticles, polymers, dielectric properties.

Introduction

Low amounts of clay in polymer-clay nanocomposite structures contribute to innovations and advances to develop some properties of polymer materials that are widely used in the industry. Very low amounts of clay or metal oxides doped into polymer matrix are instrumental in increasing the mechanical strength of polymer structures, retarding combustion properties, keeping polymer structures intact up to high temperatures, reducing gas permeability properties, inhibiting the absorption of inorganic liquids, increasing dielectric strengths and developing polymers with lower dielectric constant.[1-19]

The aim of this study is to examine in detail the dielectric properties of polymer-clay mixtures. Dielectric studies that investigate molecular drift in polypropylene-clay nanocomposites (Martin *et al.*),[2] polarization mechanism of polymeric composite obtained by mixing polypropylene and synthetic clay and electrical conductivity (Antonio *et al.*),[3] dielectric properties of thin film structures prepared according to clay concentration in poly-clay nanocomposites (Wong *et al.*),[4,5] and the effect of dispersion of clay layers in polymer chains on dielectric properties and dielectric constant of polylactide-clay (Pluta *et al.*),[6] and of polymer-clay composite constructions (Rick D. Davis *et al.*),[7] are noteworthy.

On the other hand, the interface effect significantly changes the dielectric and mechanical properties of polymer-clay nanocomposite films,[2-4,8-14] which is why different polymeric chemicals referred to as compatibilizers are used to ensure that clay

(additive material) is coordinated to the polymeric structure and homogeneously dispersed throughout the structure. This study used two different types of compatibilizers and dielectric spectroscopy method to examine the effect of clay (cloisite southern clay) on dielectric properties and relaxation behavior in the low frequency region depending on the dispersion of the clay in the polyethylene structure.

Experimental

Polyethylene-clay nanocomposite films were prepared by employing commercial grades linear low density polyethylene (LLDPE) as matrix, two different types compatibilizer and organo-clay as nanofiller. Maleic anhydride grafted polyethylene (PE-*g*-MA) and oxidized polyethylene (OxPE) were used as compatibilizer. Physical properties of components and experimental works of nanocomposites preparation route by melt processing method were previously reported by Durmus *et al.*, in detail.[20,21] It is well-known fact that the reason for using compatibilizers which generally include reactive/functional groups into their chemical structure is to increase polymer-clay interfacial interactions and dispers clay layers homogeneously into polymer matrix especially for polyolefins. Compositions of LLDPE/clay nanocomposites are also listed here, in Table 1. The structural, rheological, morphological and mechanical properties of those nanocomposites were reported by Durmus *et al.*.[20,21]

This study examined the dielectric properties and relaxation behavior, at different temperatures, of pure polyethylene (LLDPE), LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposite films.

The capacitance *C* and dielectric loss factor (tan delta) of pure LLDPE, LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites were separately measured using a Novocontrol Alfa-A high performance frequency analyzer in the frequency range of 10^{-1} to 10^7 Hz and temperature range between 273 K and 373 K. Dielectric constant (permittivity) ε' values of nanocomposite samples were derived using the relation

$$\varepsilon' = \frac{Cd}{\varepsilon_o A} \tag{1}$$

where *C* is the capacitance of the samples, *d* is the sample thickness (around 80-110 μm thin films), ε_o is electrical permittivity of vacuum and *A* is the surface area of the gold coated circular brass electrodes.

Results and Discussion

Structural characterizations of LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay composites were investigated by Durmus *et al.*. According to TEM and XRD analysis results, both compatibilizers (PE-*g*-MA and OxPE) played an important role in the dispersion of clay layers into the polymer matrix and the clay exhibited a more homogeneous dispersion in the polymer structure in LLDPE-PE-*g*-MA/clay composite samples. Melt rheology tests also indicated that structure of compatibilizer led to formation of nanocomposite morphology, interfacial interaction between clay layers and polyethylene matrix and thus dispersion of nanofiller.[20,21]

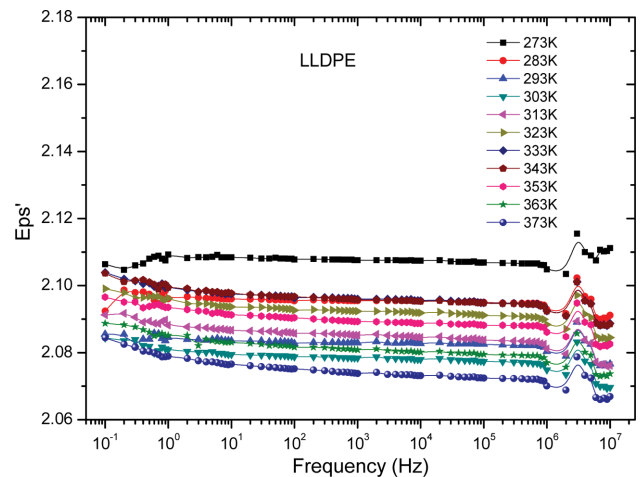Figures 1, 2 and 3 show the changes in dielectric constants

Figure 1. Dielectric constant (permittivity) of natural LLDPE as a function of frequency at different temperatures.

Table 1. Composition of Polymer-clay Nanocomposites (wt%)[20,21]

Sample	LLDPE	Compatibilizer-1 PE-g-MA	Compatibilizer-2 OxPE	Clay Phr*
LLDPE	100			
LLDPE-PE-*g*-MA/clay	85	15		5
LLDPE-OxPE/clay	85		15	5

Phr*: Parts per hundred of base matrix.

of pure LLDPE, LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites at different frequencies, respectively.

Figure 1 shows that the dielectric constant of pure polyethylene film is 2.1 and does not change with an increase in temperature and frequency, which suggests that there are no micro-sized dipolar structures that could be polarized in the structure and that the increase in temperature did not allow the formation of micro-sized dipolar structures.

Figures 2 and 3 show that the dielectric constant of both LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites is constant at around 1.5, which increases up to 4.8 and 2.8, respectively, at high temperatures. Dielectric permittivity
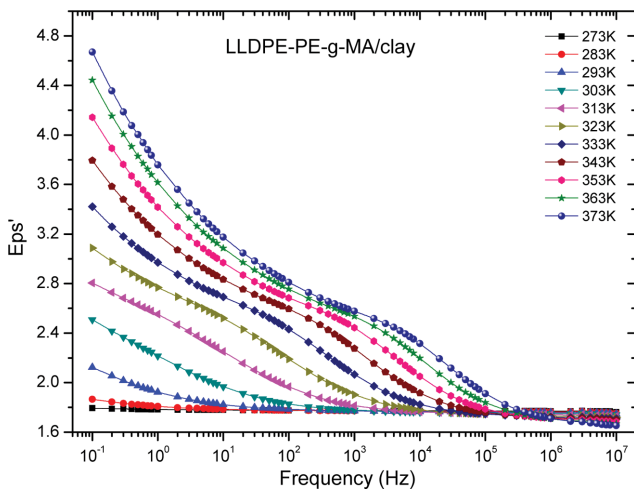
decreases and typical dielectric behavior is observed in both composites with increasing frequency.[22,23] We can state for both samples that the dipolar effect may be at play and that there may be polarization in the low frequency region especially due to an increase in load mobility in the structure with increasing temperature. Dielectric permittivity does not change significantly up to room temperature, increases systematically due to the increased temperature in the low frequency region, which is interpreted by many researchers as interplanar polarization or Maxwell-Wagner-Sillars (MWS) polarization for similar samples.[24-30]

Figures 4, 5 and 6 show the frequency-dependent changes in the loss factor (tanδ) of pure LLDPE, LLDPE-PE-*g*-MA/clay

Figure 2. Dielectric constant (permittivity) of LLDPE-PE-*g*-MA/clay nanocomposite as a function of frequency at different temperatures.

Figure 4. Dielectric loss factor of natural LLDPE as a function of frequency at different temperatures.

Figure 3. Dielectric constant (permittivity) of LLDPE-OxPE/clay nanocomposite as a function of frequency at different temperatures.
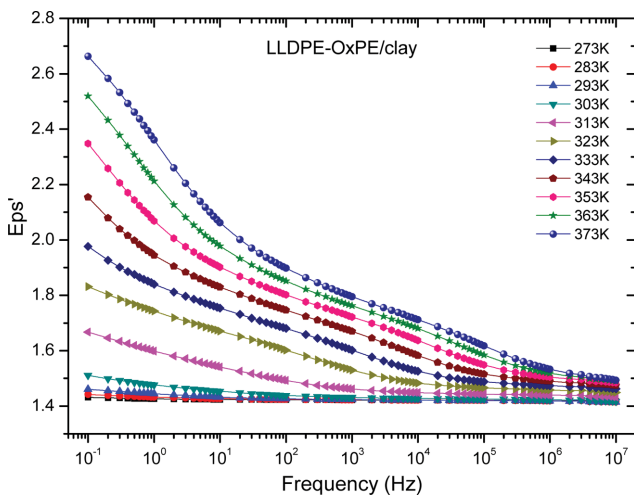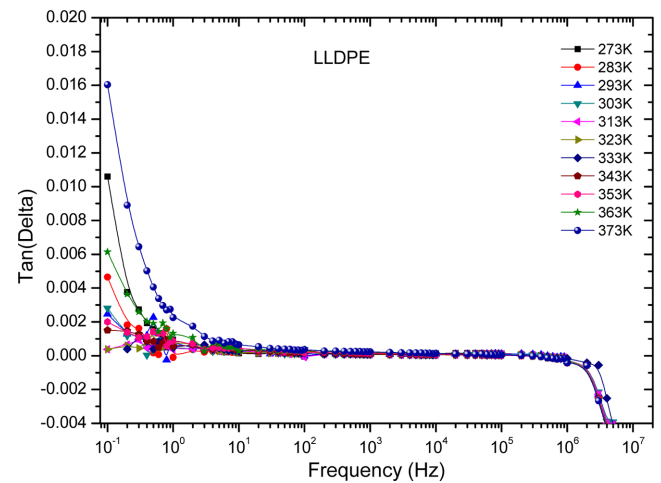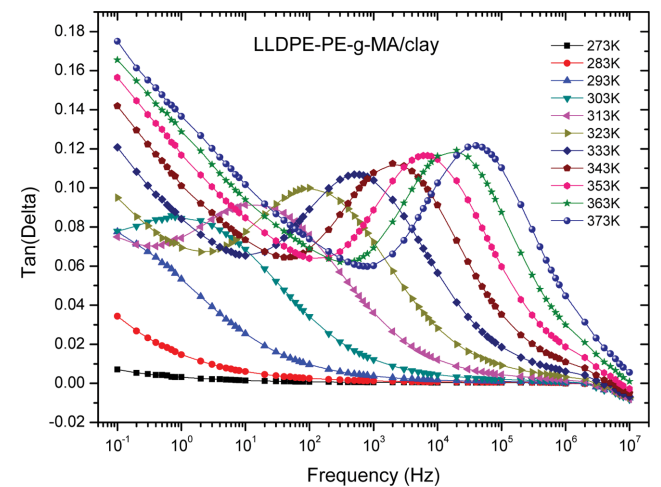

Figure 5. Dielectric loss factor of LLDPE-PE-*g*-MA/clay nanocomposite as a function of frequency at different temperatures.
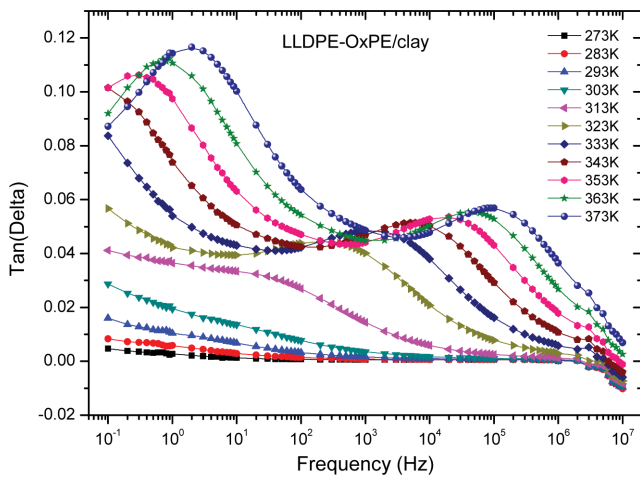
Figure 6. Dielectric loss factor of LLDPE-OxPE/clay nanocomposite as a function of frequency at different temperatures.

and LLDPE-OxPE/clay nanocomposites, respectively.

There are no significant frequency-dependent changes in the loss factor of pure LLDPE in the broad frequency range while relative increases are observed at low frequencies and high temperatures, particularly at 373 K.

In the frequency-dependent change in the loss factor of LLDPE-PE-*g*-MA/clay nanocomposite, the maximum value first observed at 303 K shifts towards higher frequency values in direct proportion to temperature, which can be interpreted in the way that there is an increase in polarization due to the load mobility of the structure with increasing temperature and that there are maximum losses in certain frequency regions.

While no loss is observed in LLDPE-OxPE/clay nanocomposite at low temperatures, two maximum values are observed especially at 353 K and higher. Unlike LLDPE-PE-*g*-MA/clay nanocomposite, a second maximum loss is observed in LLDPE-OxPE/clay nanocomposite in the low frequency region. Increasing with an increase in temperature, this maximum loss shifts towards higher frequencies. This change signifies that the structure is thermally excited by the temperature. Numerous studies have shown that polymer chain groups in composite structures can be more easily orientated by thermal excitation due to the applied field effect,[28-34] suggesting that in LLDPE-PE-*g*-MA/clay nanocomposite, DC conductivity has a significant contribution in the low frequency region due to ionic motion while it is not the case in LLDPE-OxPE/clay nanocomposite.[35] The peaks in both samples observed to shift towards high frequency indicate that the clay was not homogeneously dispersed in the structure due to the effect of the compatibilizer (OxPE) and that different polarization mech-

anisms were formed, confirming the results of the study conducted by Durmuş *et al.* on the structural characterization of LLDPE-OxPE/clay composites.[20,21]

Figures 7, 8 and 9 show the temperature-dependent changes in the dielectric constant of pure LLDPE, LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites, respectively, in the frequency range of 10^{-1}-10^6 Hz.

Figure 7 shows that the dielectric constant of pure LLDPE varies between 2.07 and 2.11 depending on the temperature at different frequencies.

Figures 8 and 9 show that the temperature-dependent variations in the dielectric constant of both LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites are similar. However,
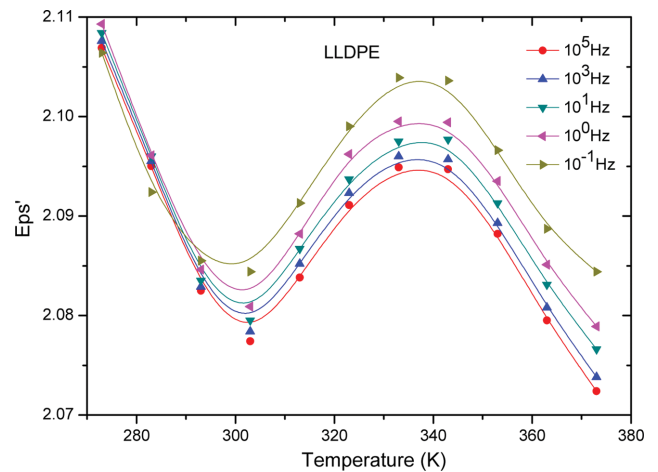

Figure 7. Dielectric constant (permittivity) of natural LLDPE as a function of temperatures at different frequencies.
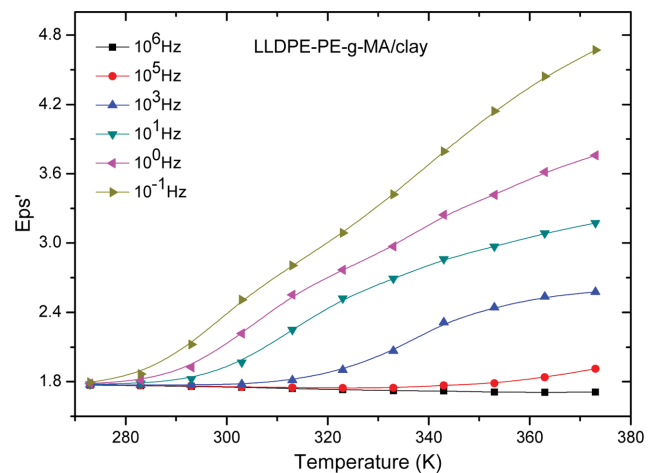

Figure 8. Dielectric constant (permittivity) of LLDPE-PE-*g*-MA/clay nanocomposite as a function of temperatures at different frequencies.
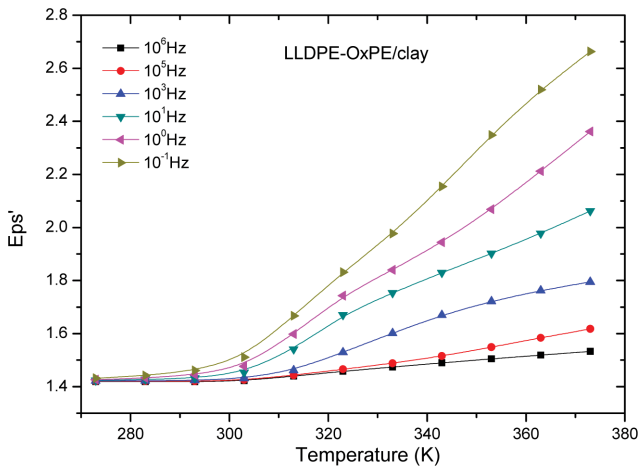
Figure 9. Dielectric constant (permittivity) of LLDPE-OxPE/clay nanocomposite as a function of temperatures at different frequencies.

Figure 10. Dielectric loss factor of LLDPE-PE-*g*-MA/clay nanocomposite as a function of temperatures at different frequencies.

Figure 11. Dielectric loss factor of LLDPE-OxPE/clay nanocomposite as a function of temperatures at different frequencies.

the dielectric constant of LLDPE-PE-*g*-MA/clay composite remains constant at 1.80 at 10^6 Hz while that of LLDPE-OxPE/clay nanocomposite shows a slight upward trend at 1.42 with an increase in temperature. For both samples, the dielectric constant increases considerably at frequencies below 10^3 Hz and at high temperatures. The dielectric constant is 4.8 and 2.8 for LLDPE-PE-*g*-MA/clay nanocomposite and LLDPE-OxPE/clay nanocomposite, respectively, indicating that the dispersion in LLDPE-PE-*g*-MA/clay nanocomposite is more homogeneous and that the charges accumulated on the clay surfaces cause a dipolar effect leading to an increase in the dielectric constant. These results, on the other hand, indicate that the dispersion in LLDPE-OxPE/clay nanocomposite is not homogeneous enough and that the clay layers cause large clustering in close proximity resulting in a lower dipolar effect and dielectric constant.[27]

Figures 10 and 11 show the temperature-dependent changes in the loss factor (tanδ) of LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites, respectively, in the frequency range of 10^{-1}-10^6 Hz.

Though the changes in the loss factors of both samples are similar, the changes at frequencies of 10^3 Hz and lower support previous results. It can be stated that the loss factor in the structure of both nanocomposites tends to increase with an increase in temperature at low frequency values. Especially the loss factor of LLDPE-PE-*g*-MA/clay composites exhibits a proportional change with dielectric permittivity.

Figures 12 and 13 show the frequency-dependent changes in the dielectric constants and loss factors of pure LLDPE,
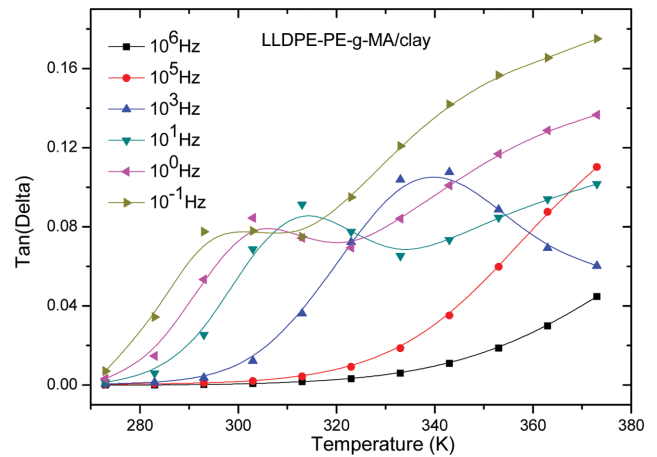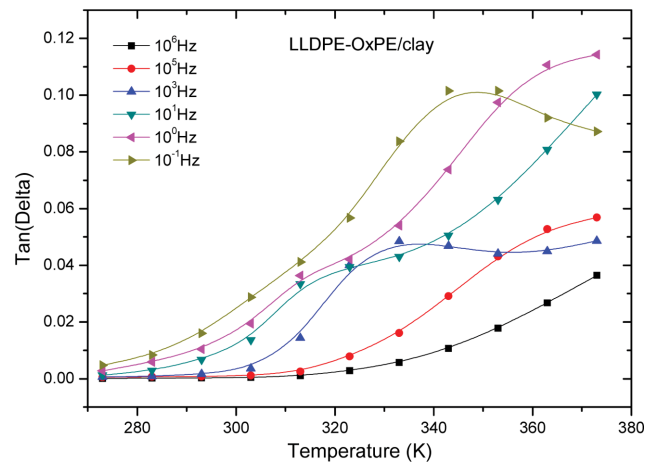
LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites at high temperatures.

Dielectric spectroscopy method was used to make comparisons in the high temperature region to determine whether clay was homogeneously dispersed. Figures 12 and 13 show that there is no significant change in the dielectric constant and loss factor of pure LLDPE due to temperature and frequency. However, there is a significant change in the dielectric constant and loss factor of LLDPE-PE-*g*-MA/clay and LLDPE-OxPE/clay nanocomposites at high temperatures and in the low frequency region. It can be argued that clay is more homogeneously dispersed in the structure of LLDPE-PE-*g*-MA/clay nanocomposite and therefore load distributions differ by the state of clay layers and that dielectric constant increases due to
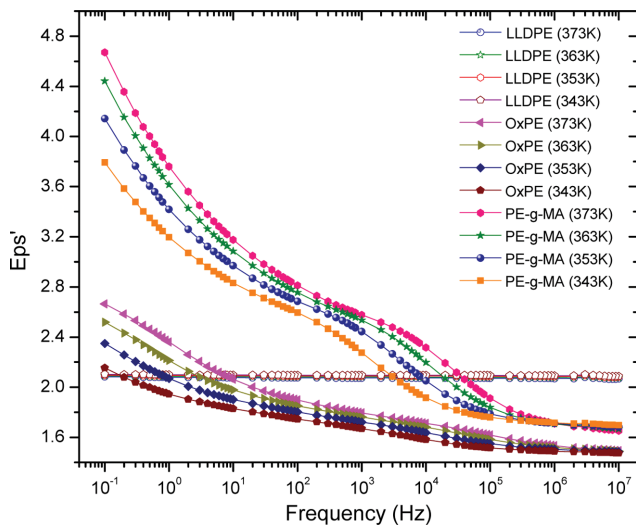
Figure 12. Dielectric constant (permittivity) of natural LLDPE and nanocomposites as a function of frequency at high temperatures.
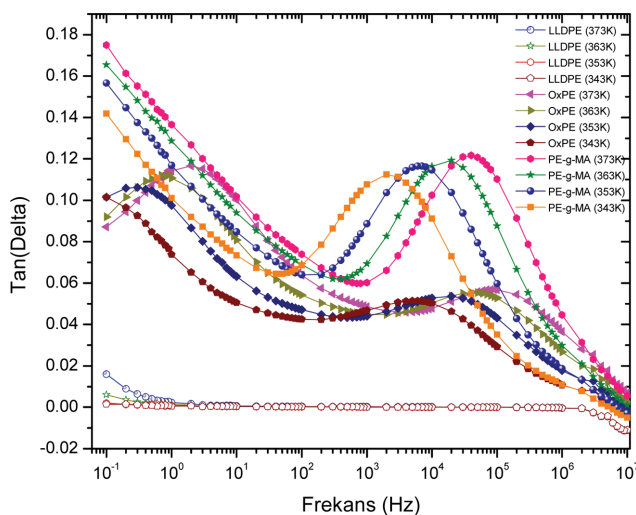

Figure 13. Dielectric loss factor of natural LLDPE and nanocomposites as a function of frequency at high temperatures.

the effect of the charge accumulated on electrodes depending on the proportional arrangement of charges on the surface. Moreover, the proportional arrangement of charges in question indicates a pronounced polarization between surfaces.[29,32,34-36] The shift of dielectric losses to the high frequency region with an increase in temperature suggests that the conductivity of LLDPE-PE-*g*-MA/clay nanocomposite is somewhat higher than that of the others.

Conclusions

Activation energies for LLDPE-PE-*g*-MA/clay and LLDPE-

OxPE/clay nanocomposites are 1.24 and 1.32 eV, respectively. These results confirm that ionic conduction is carried out by charged particles in the structure. These results also indicate that polarization exits between clay layers, which has been observed by many investigators in similar polymer materials.[6,24,37]

It can be stated that LLDPE-PE-*g*-MA/clay nanocomposite clay was homogeneously dispersed and charges accumulated on the clay surfaces caused a dipolar effect, resulting in an increase in dielectric constant. It is believed that the dispersion of the clay in LLDPE-OxPE/clay nanocomposite was not homogeneous enough and that the clay layers caused clustering in close proximity resulting in a lower dipolar effect and dielectric constant.

The temperature-dependent losses observed in the low frequency region shifted towards higher frequencies with increasing temperature. This is interpreted as the fact that polymer chain groups in LLDPE-PE-*g*-MA/clay nanocomposite structures can be more easily oriented by thermal excitation due to the applied field effect. These results are consistent with the literature.

In conclusion, homogeneous nanocomposite materials obtained using suitable compatibilizers for clay-polymer interaction will make a significant contribution to industrial applications. Furthermore, dielectric spectroscopy method can be a cheaper and faster alternative to SEM and XRD methods for structure analysis.

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