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IMPACT OF CONDUCTING POLYMER FILLER ON THE DIELECTRIC PROPERTIES OF NYLON 11

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Abstract. The dielectric studies of semi-crystalline Nylon 11 filled with a conducting polymer (PANI) were investigated in a wide range of frequency and temperature by using Impedance Analyzer. The main focus was on the effects of conducting filler content on dielectric properties of Nylon 11. The prominent factors such as dielectric permittivity, loss factor, and loss tangent were studied at high frequency. Two different concentrations (1 % and 5 % w/w) of the conducting filler were used. It was observed that with the increase of fillers concentration, the value of dielectric permittivity (ε'), the dissipation factor (ε") and loss (tan$d$) decrease compared to pure Nylon 11.

Key words: Nylon 11, filler, dielectric property, polyaniline.

1. Introduction

The odd nylons which have an odd number of carbon atoms between the amide groups in the main chain, [–NH–$(CH_2)_x$–CO]$_n$, are an interesting class of polymers. The odd nylons possess intramolecular alignment of the large dipole moment of the amide group (3.7D) in the same direction [1, 2]. Many studies have demonstrated the great stability of Nylon 11 in electroactive properties at high temperature. Thus the investigation of dielectric properties of Nylon 11 at temperatures higher than *Tg* is of particular interest both from the academical and technological point of view.

Dielectric properties of the polymer are closely related to chemical and crystalline structure of materials and the dipole density in the crystalline unit cell. All *trans*-conformations of the odd nylon molecules give a large dipole moment perpendicular to the axis and all dipole moments are aligned to the same direction. So the odd nylons can have a spontaneous polarization in the unit cell of the crystalline phase and thus the Nylon 11 is a good piezoelectric material. It has been reported that Nylon 11 has tri-clinic a and pseudo-hexagonal g-form [3]. Gang Wu *et al*. [4] reported that dielectric permittivity of Nylon 11 (g -form) specimen was higher than that of Nylon 11 (a -form).

Takase *et al*. [5] studied the dielectric properties of poled and annealed samples of Nylon 11 at higher temperatures up to the respective melting points. Ionic conduction was found to dominate the dielectric behaviour above *Tg*.

In order to assess the potential application of Nylon 11 for high frequency transducers, sensors and other applications, it is necessary to study the basic dielectric properties and their relationship with the structure and morphology of Nylon 11. It was therefore thought interesting to undertake the measurements of dielectric properties of Nylon 11 filled with PANI powder. The change in the dielectric behavior due to addition of PANI filler has been investigated for two different concentrations, *i.e.* 1 % and 5 % w/w PANI.

Literature survey for filled polymers has been carried out and almost all the work is concentrated upon the studies of electrical conductivity of filled polymers [6-8]. Further it is observed that polymers filled with conducting fillers show a drastic increase in electrical conductivity above critical concentration (f_c). Hence in the present work the concentration was kept low, so that under filled conditions, samples will not give high electrical conductivity. Hence the concentration of the added PANI powder was kept low, *i.e.* 1 % and 5 % (w/w).

In the present case the aim was to increase the dielectric properties of filled Nylon 11 and hence low concentrations of semi-conducting fillers have been selected.

2. Experimental

Nylon 11 (Sigma Aldrich CHEMIE GmbH, Germany) in the form of beads was used in the preparation of samples. Samples of pure and PANI filled (1 % and 5 %, w/w) Nylon 11 were prepared in the form of circular discs using hot press molding. The thickness of the circular discs was 1.5 mm. For dielectric measurements the samples were coated with gold on both sides (circular, S in. diameter) by vacuum deposition (10^{-7} Torr).

Polyaniline (PANI) was chemically synthesized in the laboratory using potassium dichromate ($K_2Cr_2O_7$) as an oxidizing agent and H_2SO_4 as an acidic medium [9]. The salt form of PANI was prepared in the form of powder and was used as fillers.

Two terminal electrode systems with an Impedance Analyzer (HP 4192A) were used. The dielectric permittivity was measured as a function of frequency (range of 10^2–10^7 Hz) and temperature (range 293–393 K). The temperature was being controlled by means of a Honeywell BC 1010 programmable temperature controller with precision of $\pm$274 K over the entire measurement range. The experimental error in dielectric parameters was 0.5 % and 1.5 % for ε' and ε'', correspondingly.

The real part of the dielectric permittivity (ε') and the loss (tanδ) were obtained experimentally, while imaginary part was evaluated using the relation $\frac{e''}{e'} = \tan d$.

2.1. Wide Angle X-Ray Diffraction (WAXD)

WAXD is a widely used technique to study the crystallinity of a polymer. Phillips Diffractometer with CuKα radiation was used in this study. The wide angle X-ray diffraction of pure and filled Nylon 11 was recorded at room temperature with 1^0/min scan over the range of 2q from 15^0 to 40^0.

From the radial scans of intensity *versus* 2q, the lateral order or crystallinity index was determined using Manjunath's formulae [10].

3. Results and Discussion

3.1. Temperature Dependence of ε' and ε''

Graph is plotted between ε', ε'' with respect to temperature in the range of 293–393 K for 100 KHz (Fig. 1a). It has been observed that ε' increases with the increase of temperature.

For low temperatures (293–323 K), Fig. 1a shows that addition of PANI in pure Nylon 11 (1 % and 5 % w/w) has a negligible effect on dielectric permittivity (ε'). But the value of ε' increases with the increase of temperature for all the samples for the temperature above 323 K. With temperature increase above 328 K, sharp difference in value is observed.

From Fig. 1a, overall study reveals that addition of PANI in Nylon 11 decreases the value of dielectric permittivity (ε') as compared to pure Nylon 11.

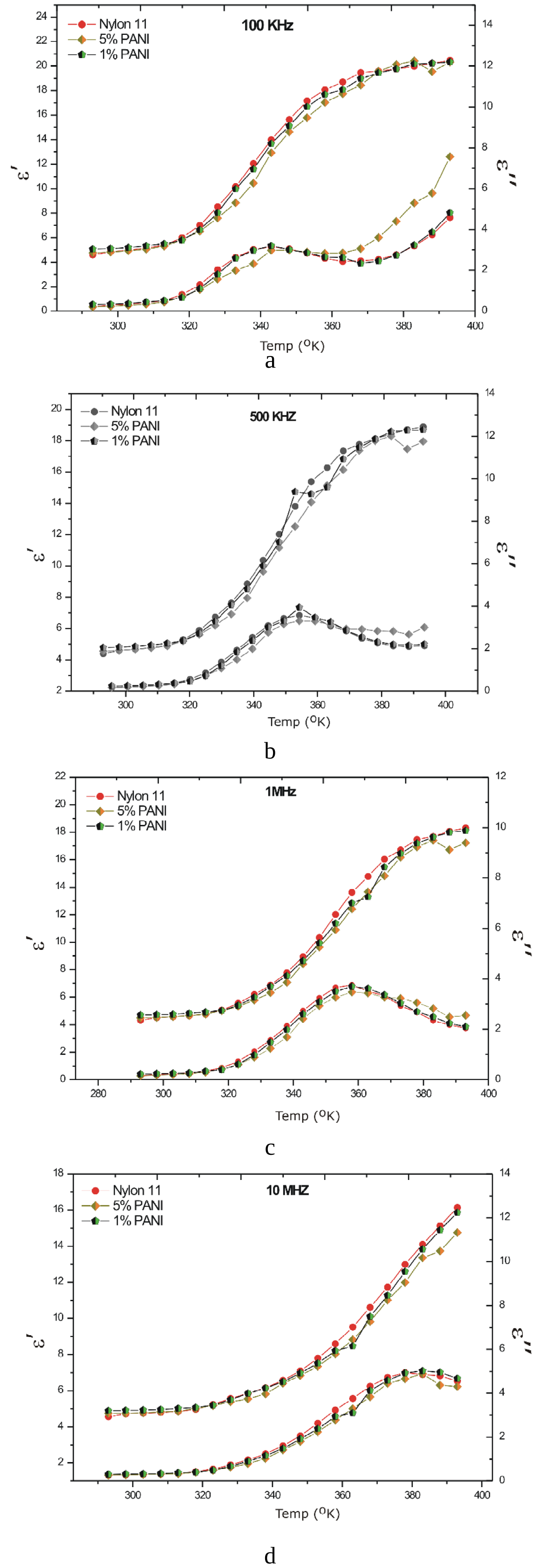

Fig. 1. Temperature dependence of ε' and ε'' for pure and PANI filled Nylon 11 at different frequencies

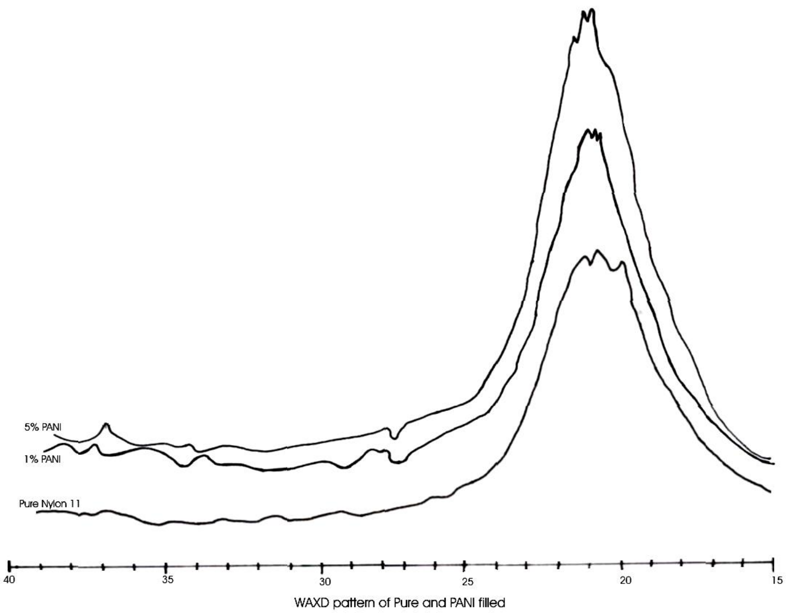

Fig. 2. X-ray scans for the pure and PANI filled samples

At 373 K, the value for all samples becomes equal to *i.e.* 20.341. This trend continues for higher temperatures up to 393 K.

From Fig. 1a, the value of dielectric loss factor ε'' is almost equal for all samples at low temperature up to 318 K. It has been observed that with the increase in temperature above 318 K, the ε'' values also increase but they are different for pure and 5% PANI filled Nylon 11.

As the temperature increases, a peak appears near 343 K. The ε'' value for pure and PANI filled Nylon 11 is almost the same.

At very high temperature ε'' increases sharply for 5% PANI filler as compared to pure and 1% PANI filled Nylon 11. From Fig. 1a it is observed that at very high temperature the ε'' value for 1% PANI filled Nylon 11 is close to pure one.

In Figs. 1b and c (for 500 KHz and 1 MHz) almost similar features are observed for all the three samples. Variation of ε' for pure and PANI filler with temperature is almost identical. At 378 K the value at 500 KHz for all samples is identical, *i.e.*18.103, while for 1MHz is 17.642 at 383 K.

Variation of ε'' for all samples is almost similar. It has been observed from the graph that a peak appears at 353 K for 500 KHz and around 358 K for 1 MHz.

From Fig. 1d (for 10 MHz), it has been observed that at low temperatures (293–323 K) dielectric permittivity increased with addition of PANI contents in pure Nylon 11. The ε' value almost coincides with pure and PANI filled Nylon 11 at 323 K. As the temperature increases above 323 K the curves split from each other, wherein the ε' value is maximum for pure Nylon 11 as compared to PANI filler.

Thus it has been observed that the dielectric permittivity (ε') at very high frequencies (10 MHz):

Nylon 11 > 1% PANI Filler
> 5% PANI filler at all temperatures

Thus the impact of the addition of conducting polymer filler (PANI) in the pure Nylon 11 resulted into a decrease of the dielectric permittivity (ε').

Fig. 2 shows the X-ray scans for pure and PANI filled samples. The X-ray scan of pure Nylon 11 shows three small peaks, two peaks at $2q = 20°$ & $20.8°$ corresponds to α crystal form and the third peak at $2q = 21.2°$ corresponds to γ form.

Due to addition of 1% PANI in pure Nylon 11, three intense peak appears at $2q = 21.0°$, $2q = 21.2°$ and $2q = 21.4°$, which corresponds to γ form. Thus shifting of peaks indicates a partial change of the structure from α to γ-form.

At further increase of the concentration (*i.e.* from 1% to 5%) of PANI in pure Nylon 11, there is an increase of γ peaks intensity and the peak slightly shifts to a higher angle, *i.e.* $2q = 21.6°$, $2q = 21.8°$ and $2q = 22°$.

Thus by addition of PANI as a filler in pure Nylon 11, the WAXD studies show that there is a phase transition from α to γ -form.

It has been already reported from WAXD and FT-IR that there is a slight crystal modification due to the addition of PANI fillers in pure Nylon 11 [11]. It has been reported that pure Nylon 11 exhibits both α and γ crystalline form, whereas by addition of PANI in pure Nylon 11 phase transition α→γ takes place.

In polymers the dielectric property is closely related to the chemical and dipole density in the crystalline unit cell and the odd nylons can have spontaneous polarization in the unit cell of a crystalline phase. It has been reported that Nylon 11 exists in two crystalline forms: a triclinic α- and pseudo hexagonal γ-form [3]. Similarly Gang Wu *et al.* [4] studied the dielectric behavior of Nylon 11 films in α-and γ-forms at 10 Hz and reported that dielectric permittivity of Nylon 11 (γ-form) was higher than that of Nylon 11 (γ-form). Several researchers [12-17] attributed the above results to the effective field induced dipole alignment in the γ structure than in the ordinary structure.

The study of dielectric property of metal filled Nylon 11 has also been carried out and reported [11]. The result obtained exhibits similar tendency as mentioned earlier.

But in the present case interesting results have been obtained. The structural analysis of PANI filled samples reveals complex formation between Nylon 11 and polyaniline. Thus addition of PANI in Nylon 11 transforms Nylon 11 into a new material having structural properties reported elsewhere [11]. Hence the comparison between γ structures in PANI filled with mixture of both α and γ structure in pure Nylon 11 would not be appropriate. Further PANI is in a salt form having conductivity 10^{-4} S/m, which lies in a semiconducting range. Ching Piou *et al.* [18] reported that polyaniline can have the high level of conductivity and permittivity and these properties can be tuned easily and precisely by blending with conventional polymers. This may be one of the reasons affecting the dielectric permittivity values and reducing them to lower values as compared to pure Nylon 11.

Variation of ε'' at 10 MHz is almost identical up to 348 K for all three samples. The ε'' value increases with the increase of temperature. A peak appears at around 383 K for PANI filled samples while for pure Nylon 11 it appears at 378 K.

At very high temperatures in the range of 383–393 K, the value of dissipation factor ε'' is for 1% PANI filler > Nylon 11 > 5% PANI filler.

One can see from Fig. 1 that at high frequency the dissipation factor ε'' increases with the use of conducting polymer filler like polyaniline. However ε' decreases as the concentration of fillers increases in comparison with Nylon 11.

In case of dissipation factor (ε''), with the increase of frequency, the peak shifts towards higher temperature and the ε'' value for pure Nylon 11 is less as compared to filled samples (1% and 5% w/w PANI). The dissipation factor (ε'') is greater for filled samples than for pure Nylon 11 at frequency range (100 KHz–1 MHz). But at very high frequency (10 MHz) and temperature (393 K) the dissipation factor is for 1% PANI filler > Nylon 11 > 5% PANI filler.

3.2. Frequency Dependence of ε'' and tan d

The graph of dielectric permittivity ε' as a function of frequency over a wide range (0.005 –13 MHz) for pure and PANI filled Nylon 11 at room temperature has been studied. It has been observed that ε' remains almost constant in the frequency range of 5–10MHz for all three samples. Thus it has been observed that the dielectric permittivity ε' with respect to frequency is: 1% PANI filled < Nylon 11 < 5% PANI filled.

The ε' at room temperature at all frequencies depends upon the concentration of fillers. It is also evident from Wide Angle X-ray Diffraction that both pure as well as filled samples have γ structure. And the crystallinity of the filled samples has not reduced much from pure Nylon 11.

It has already been reported [11] that due to addition of PANI, totally new structures are getting developed for both the concentration of PANI, therefore we cannot co-relate the structural behaviour as well as dielectric properties of the filled samples with the pure Nylon 11. The characteristics of original polymer completely changed due to the formation of the complex structure which could also be revealed through WAXD. Thus the results indicate that by addition of PANI in pure Nylon 11, the crystal transformation takes place, *i.e.* α→γ-phase.

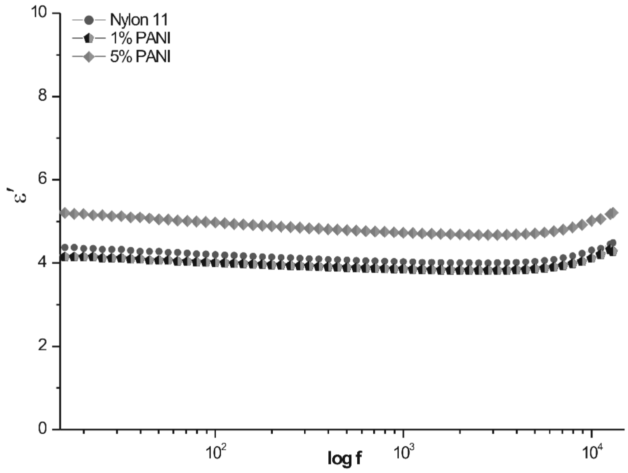

Fig. 3. Frequency dependence of ε' for pure and PANI filled Nylon 11 at room temperature

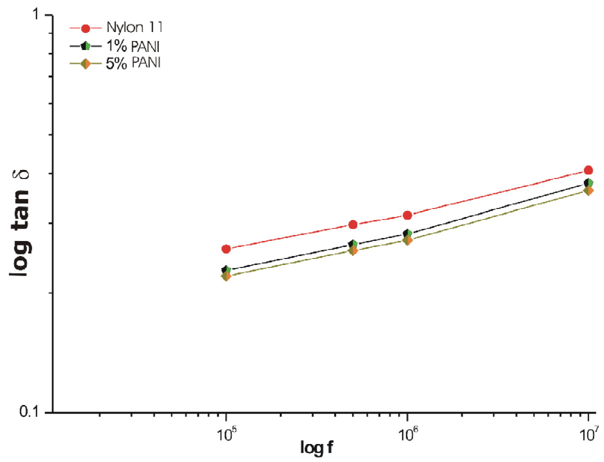

Fig. 4. Logarithmic plot of tan δ as a function of frequency for pure and PANI filled Nylon 11

Thus the above discussion reveals that due to addition of a conducting filler (*i.e.* PANI) in an insulating material (*i.e.* Nylon 11), a complex structure has been developed, which induces crystal transformation $\alpha \rightarrow \gamma$-phase. However these changes could not be compared with the original insulating material (*i.e.* Nylon 11).

Fig. 3 shows the frequency dependence of dielectric loss (tan δ) for pure and PANI filled Nylon 11. It shows that dielectric loss increases with the increase of frequency for all three samples.

Fig. 4 shows a plot of $\tan\delta_{max}$ *versus* log *f* for all three samples at room temperature. The graph is a straight line having nearly equal slope for all the three lines corresponding to these samples.

From the same Fig. 4 it may be observed that the $\tan\delta_{max}$ value decreases by addition of PANI powder. The decrease of $\tan\delta_{max}$ height indicates the decrease of an amorphous content in the sample. In other words, there is more the crystalline content in a sample, the less is the height of $\tan\delta_{max}$. Similar results for PANI filled samples have been obtained in respect to the crystalline content of PANI filled Nylon 11 and have been investigated using WAXD analysis.

4. Conclusions

The effect of addition of PANI powder in Nylon 11 on the dielectric permittivity has been explored. It was found that the addition of PANI 1 % and 5 % (w/w) induces complete structural modification as compared to pure Nylon 11.Therefore the reduction of the dielectric permittivity *e*' can also be attributed to the structural modification. However the results obtained in PANI filled samples cannot be compared with pure Nylon 11 as the entirely new structure has been formed by addition of PANI which does not resemble a pure Nylon 11.

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ВПЛИВ ПРОВІДНИХ ПОЛІМЕРНИХ НАПОВНЮВАЧІВ НА ДІЕЛЕКТРИЧНІ ВЛАСТИВОСТІ НАЙЛОНУ 11

Анотація. *В широкому інтервалі частот і температур, з використанням імпедансного аналізатора, досліджено діелектричні властивості напівкристалічного Найлону 11, наповненого провідним полімером (ПАНІ). Головна увага була звернута на вплив концентрації провідного полімеру на діелектричні властивості Найлону 11. При високих частотах вивчали такі чинники, як діелектрична проникність, коефіцієнт втрат і тангенс кута діелектричних втрат. Досліджено дві різні концентрації наповнювача: 1 і 5 % мас. Визначено, що з підвищенням концентрації наповнювача величини діелектричної проникності, коефіцієнт розсіювання і тангенс кута втрат зменшуються порівняно з чистим Найлоном 11.*

Ключові слова: *Найлон 11, наповнювач, діелектричні властивості, поліанілін.*