10.1. Introduction

The development of polymers has replaced the conventional insulating materials such as glass, wood, asphalt, mica, amber and related materials. Most of the polymers are excellent insulating materials and they are less susceptible to conduction by imperfection and structural irregularities, which made them an attractive choice for electrical applications. Blending offers the possibility of combining the unique properties of available polymers and thus of producing materials with tailor made properties, which often has advantages over the development of completely new polymeric materials [1,2]. Studies on electrical properties of polymer blends have been reported by several researchers [3-17]. Investigation of dielectric properties of polymers is essential since large volumes of polymeric materials are used for electrical applications. According to different studies, the dielectric properties of polymers and blends depend upon crystallinity, structure, morphology and presence of fillers. The dielectric properties of polymer blends are found to depend upon the effective moment of the system. Dielectric properties of several polymer blends including thermoplastic elastomers (TPE) have been analysed by our research group [18-22].

The present chapter is devoted to the analysis of dielectric properties of PA/PS blends. Even though PA is widely used for insulating purposes, it exhibits sufficiently high value of dielectric
constant and hence low resistivity. Nylons have a major drawback that it absorbs moisture, which again is a demerit for the polymer to be used for electrical applications. Our studies regarding the water sorption behaviour of PA (chapter 9) suggested that, blending with PS diminishes the water sorption behaviour, which is further reduced upon compatibilisation. Therefore, blending of PA with a non-polar polymer such as PS is expected to improve the dielectric performance of PA, by reducing the polarity as well as the moisture uptake of the blends. This chapter presents the results of our studies on the dielectric properties of PA/PS blends. Special attention has been paid to analyse the effect of blend composition and the influence of compatibilisation using SMA 8 copolymer on the dielectric properties of PA/PS blends.

10.2. Results and Discussion

10.2.1. Uncompatibilised blends

10.2.1.1. Volume resistivity

The most desirable property of an insulator is its ability to resist the leakage of current. Therefore resistivity measurements are significant in the case of insulating materials. The volume resistivity of neat polymers and the binary blends are shown in Figure 10.1.
Figure 10.1: Volume resistivity ($\rho_v$) of PA, PS and their blends as a function of frequency

It can be seen from Figure 10.1 that PS, which is a good insulator possess maximum resistivity. With the incorporation of PA, comparatively a less insulating material reduces the volume resistivity. This can be explained on the basis of phase morphology of the uncompatibilised system and is discussed in chapter 3. It was found that in N20 blends PS forms the continuous phase whereas PA forms the continuous phase in N80 system. N50 exhibits a co-continuous morphology in which both the components are continuous in nature. It can be noted that the blends reflects the property of the matrix phase. In N20 blends where PS forms the matrix, the curve is very similar to PS and in N80 the case is reversed. Therefore blends with PS as the continuous phase exhibits higher resistivity. In the case of PS and PS rich blends a reduction in $\rho_v$ is observed with increase in frequency. This can be attributed to the increase in molecular mobility at high frequencies. The effect is well pronounced in the case of systems where the amorphous PS forms a continuous phase. When PA forms major phase, the matrix being comprised of a semi crystalline polymer, the
frequency variation causes little or no effect. The effect of PA content on $\rho_v$ of the blends at 1000 Hz is plotted in Figure 10.2 (frequency 1 kHz) which shows that as the PA content increases, the resistivity decreases. A change in slope is observed at 50wt % PA, which can be attributed to the phase inversion at this composition.

![Figure 10.2: Effect of blend composition on the volume resistivity.](image)

**Figure 10.2:** Effect of blend composition on the volume resistivity.

### 10.2.1.2. Dielectric constant:

The main function of an insulator is to insulate the current carrying conductors from each other and from the ground, which requires materials with very low dielectric constant. The variation of dielectric constants ($\varepsilon$) as a function of frequency for neat polymers and uncompatibilised blends are shown in Figure 10.3.
**Figure 10.3:** Dielectric constant ($\varepsilon$) of PA, PS and their blends as a function of frequency

The figure shows that PS, which is a good insulator exhibits the lowest value; while the polar PA exhibits the maximum value for dielectric constant. Dielectric constant of a material arises due to polarisation of molecules and it increases with increase in polarisability. The different types of polarisations possible in a material are those arising from (a) electronic polarisation (b) atomic polarisation and (c) orientation polarisation [23]. For heterogeneous materials, there is also the possibility for interfacial polarisation that arises due to the differences in conductivities of the two phases [24]. Therefore in the case of PA, which is a polar polymer, at low frequencies all the four types of polarisation contribute towards the dielectric constant. As a result, PA exhibits high dielectric constant, especially at low frequencies. With increase in frequency at first the interfacial contribution vanishes followed by orientation polarisation, which in turn reduces the dielectric constant at higher frequencies. Nada et al. [12] in their studies on cellulose/polyethylene glycol (PEG) blends reported the decrease in dielectric constant with frequency to dielectric
dispersion due to the lag of the molecules behind the alternation of the
electric field at higher frequency. The effect of blend composition on the
dielectric constant is shown in Figure 10.4 (frequency 1 kHz).

Figure 10.4: Effect of blend composition on dielectric constant.

The figure shows that the incorporation of PA increases the dielectric
constant of the system, which can be attributed to the increase in overall
polarity of the system with the addition of PA. Increase in dielectric
constant upon the incorporation of polar polymers was reported in literature
[19, 25]. The dielectric constant depends on resistivity by the equation [26].

\[
\log R_{10}(298K) = 23 - 2 \varepsilon(298K) \tag{10.1}
\]

(i.e., the electrical resistance of polymers decreases exponentially with
increasing dielectric constant). As suggested earlier, with the incorporation
of PA, the polarity of the system increases, which increase the orientation
polarisation as well as the interfacial polarisation that result in the increase
in \( \varepsilon \) and a decrease in resistivity (Figure 10.1). It should be noted that as the
PA content increases, it becomes the continuous phase and the blends then
Dielectric Properties

reflects properties close to that of PA. Thus N20 blends have low and N80 blends have high \( \varepsilon \) values. N50 with a co-continuous morphology possesses an intermediate value.

### 10.2.1.3 Comparison with theory

Experimental dielectric data can be compared with theoretical predictions. The dielectric constant of a composite containing two components can be expressed in the general form:

\[ \varepsilon_c = V_1 \varepsilon_1 + V_2 (1-V_1) \quad (\text{Model 1}) \]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are dielectric constants of components 1 and 2, and \( V_1 \) and \( V_2 = 1 - V_1 \) are the volume fractions of components 1 and 2, respectively. The logarithmic variation of dielectric constant can be expressed by the equation:

\[ \log \varepsilon_c = V_1 \log \varepsilon_1 + (1-V_1) \log \varepsilon_2 \quad (\text{Model 2}) \]

The dielectric constant of two-phase mixtures based on spherical particle, which consider all the possible interaction, could be calculated using the following equation [27].

\[ \varepsilon_c = \frac{1}{4} \left( \frac{H}{(H^2 + 8 \varepsilon_1 \varepsilon_2)^{1/2}} \right) \quad (\text{Model 3}) \]

where \( H = (3 V_1 - 1) \varepsilon_1 + (3 V_2 - 1) \varepsilon_2 \)

The Maxwell-Wagner-Sillars equation could be used to predict the \( \varepsilon' \) values and is given as [28]

\[ \varepsilon_c = \frac{2\varepsilon_2 + \varepsilon_1 + 2 V_1 (\varepsilon_1 - \varepsilon_2)}{2\varepsilon_2 + \varepsilon_1 - V_1 (\varepsilon_1 - \varepsilon_2)} \quad (\text{Model 4}) \]
Figure 10.5: Comparison of experimental values obtained for $\varepsilon$ with theoretical predictions

Experimentally obtained dielectric constants (at a frequency 1 MHz) for the various blends were compared with theoretical models. The comparison is depicted in Figure 10.5, which shows that experimental values deviate from all the models except model 1. It can be suggested that, the overall polarity of the system and hence the blend composition contributes more towards the dielectric constant rather than the interfacial adhesion. Therefore the model [1] which directly calculates the blend property based on the composition of component phases shows good agreement with the experimental observation. Maximum deviation from the models is shown by N50 blends. The deviation at this particular composition can be attributed to the co-continuous nature of the blends at 50/50 composition as discussed in chapter 3.

In electrical applications, it is desirable to keep the electrical losses to a minimum. Electrical losses indicate the inefficiency of an insulator. Dissipation factor (loss tangent) is a measure of the alternating current
electrical energy, which is converted to heat. This heat raises the temperature and accelerates deterioration of the polymeric materials. The variation of dissipation factor (tan\(\delta\)) and loss factor (\(\varepsilon''\)) with frequency for the various blend compositions are given in Figures 10.6 & 10.7 respectively.

**Figure 10.6:** Variation of dissipation factor of PA, PS and their blends as a function of frequency

**Figure 10.7:** Effect of frequency on the loss factor of uncompatibilised blends
The dissipation as well as loss factor increase with PA content. A relaxation region is observed in the frequency range of 10 kHz to 1 MHz, which may be due to the lag in dipole orientation behind the alternating electric field. Figure 10.8 show that the magnitude of dissipation factor increases with PA content. As the PA content increases, more dipoles are incorporated into the system that leads to a lag in the orientation of the dipoles upon the application of electric field. The variation of tanδ and ε" with PA content (at 3 kHz) is represented in Figure 10.8.

![Figure 10.8: Effect of blend composition on tan δ and loss factor.](image)

**10.2.2. Compatibilised Blends**

Since PA is a polar polymer and PS is a simple hydrocarbon polymer, PA/PS blends are immiscible. This often results in inferior properties of the blends. Hence a reactive route was employed to compatibilise the system using polystyrene –co-maleic anhydride (SMA8)
as the compatibiliser. The amine end groups of the PA will react with the anhydride groups of SMA 8 forming a graft copolymer that can locate at the interface. Analysis of phase morphology, mechanical, rheological and viscoelastic properties proves that SMA8 could act as an effective interfacial modifier in PA/PS system. In this context we analysed the effect of compatibilisation using SMA8 on the dielectric properties of N80 blends.

10.2.2.1. Volume Resistivity

The effect of compatibilisation on the volume resistivity of N80 blends is shown in Figure 10.9.

![Figure 10.9: Effect of compatibiliser concentration on the resistivity as a function of frequency.](image)

It can be observed from the figure that the initial addition of 0.5% of SMA8 resulted in a substantial increase of volume resistivity. The enhancement in volume resistivity was obtained up to 1% addition of the compatibiliser. Further addition of the compatibiliser showed a decrease in
the \( \rho_v \) values of the blends. SMA 8 is copolymer of styrene with 8% maleic anhydride content. Due to the presence of the maleic anhydride groups, the copolymer is extremely polar. During the initial addition, the anhydride groups will react with the amine groups of PA, contributing towards the reduction in overall polarity of the system. When the concentration of the compatibiliser increases, the amount of the polar groups in the system increases, and consequently the dielectric properties gets deteriorated. This is reflected as an increase in volume resistivity at high compatibiliser loading. With the incorporation of 4% SMA, the resistivity becomes almost close to that of the uncompatibilised blends. The morphology and mechanical properties of the compatibilised system suggested that by the incorporation of 2% SMA8, the CMC is reached (chapters 3&4). Therefore, further addition of compatibiliser will lead to the formation of micelles. When 4% SMA8 is added, it is expected that the system contains micellar aggregates of the compatibiliser. This in turn will result in increase in polarity and hence will decrease the volume resistivity.

**10.2.2.2. Dielectric constant**

The effect of compatibilisation on the dielectric constant of N80 blends is measured and the results are given in Figure 10.10.
It is well evident from the figure that compatibilisation resulted in a reduction of dielectric constant, which implies that the insulating property of the material can be improved upon compatibilisation. The lowest value for the dielectric constant was observed at 1% SMA8 addition. Further addition of the compatibiliser increased the dielectric constant. As discussed earlier, this observation may be due to the increase in polarity of the system with high concentration of SMA8 and the formation of aggregates of the compatibiliser beyond its CMC.

The variation of dissipation factor (tanδ) and loss factor (ε") on compatibilisation is shown in Figure 10.11 &10.12 respectively.
Figure 10.11: Effect of compatibiliser concentration on the tan δ as a function of frequency

Figure 10.12: Effect of compatibiliser concentration on the dielectric loss as a function of frequency

The effect of compatibilisation on dissipation as well as loss factor is pronounced only at high frequencies. Beyond 10 kHz, the loss factor of
compatibilised blends is lower than that of the uncompatibilised blends. The loss factor reaches a minimum at 2% loading of the compatibiliser, while further addition of SMA 8 increased the loss factor. Dissipation factor also exhibited the same trend. Increase in loss factor and dissipation factor at high concentration of SMA8 can be attributed to the increase in the polarity of system at high loadings.

10.3. Conclusion

Dielectric properties of PA copolymer, polystyrene and their blends were analysed in the frequency range from 50Hz to 5MHz. PS, which is a simple hydrocarbon polymer exhibited good insulating properties as compared to the polar PA. Between the neat polymers, PS possessed the maximum volume resistivity and minimum dielectric constant. The values for the blends fall in between the component polymers. With the increase in PS content, the dielectric constant decreased and the volume resistivity increased. When PA forms major phase, the matrix being comprised of a semi-crystalline polymer, the frequency variation causes little or no effect whereas in the case of PS rich blends; a reduction in volume resistivity was observed which can be due to the increase in molecular mobility at high frequencies. The incorporation of PS decreased the dielectric constant of the system, which can be attributed to the decrease in overall polarity of the system with the addition of PS. As the PA content increases, more dipoles are incorporated into the system that leads to a lag in the orientation of the dipoles on the application of electric field, which reflected as an increase in the magnitude of dissipation factor with increase in PA concentration. Since PA and PS form immiscible blends SMA8 was added to compatibilise the blends. In this case compatibilisation takes place through
the interfacial chemical reaction between the anhydride groups of SMA copolymer and amine end groups of PA. It was observed that compatibilisation increased the volume resistivity of PA/PS blends. The enhancement in volume resistivity was obtained up to 1\% addition of the compatibiliser. Beyond that, the addition of compatibiliser showed a decrease in the $\rho_v$ values of the blends. This may be due to the fact that, at higher concentrations of SMA8, amount of the polar groups in the system increases, and consequently the dielectric properties gets deteriorated. Similar results were obtained for dielectric constant. The lowest value for the dielectric constant was observed at 1\% SMA8 addition. Effect of compatibilisation on dissipation as well as loss factor is pronounced only at high frequencies. The dissipation as well as the loss factor reached a minimum at 2\% loading of the compatibiliser, while further addition of SMA 8 increased the loss factor. Increase in loss factor and dissipation factor at high concentration of SMA8 can be attributed to the increase in the polarity of system at high loadings.

10.4. References


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