CHAPTER 8:

ELECTRICAL PROPERTIES

ABSTRACT

The electrical properties of TPU and PP blends are presented in this chapter. Special attention has been paid to analyze the effect of blend ratio, compatibilisation and effect of nanoclay on the electrical properties of TPU/PP blends. The electrical properties measured were dielectric constant ($\varepsilon'$), volume resistivity ($\rho_v$), loss factor ($\varepsilon''$) and dissipation factor (tan$\delta$).

The results discussed in this chapter have been submitted for publication in Journal of Materials Science.
8.1 Introduction

The electrical properties of polymer cover an extremely diverse range of molecular phenomena. Many of the TPEs have found extensive application as dielectric materials in cables and capacitors. Polymeric insulators are widely used due to their superior service properties in the presence of heavy pollution and wet conditions, and also very desirable characteristics from the observation point of transportation (no damage at transportation) and framing (lower weight) compared to the porcelain glass insulator [1-4]. A complete understanding of the dielectric properties such as dielectric constant and loss factor as a function of frequency and temperature is often necessary for the proper selection of polymers as insulating materials and to gain an insight into the nature of their electrical response [5].

In TPEs the rubber phase can be made conductive by the addition of conductive fillers [6-8]. Vulcanisation is used to crosslink the rubber molecule chains to form an elastic network. Vulcanisation increases the retractable force resulting from a large deformation and reduces amount of permanent deformation remaining after the deforming force.

Electrical properties of various polymer blends have been investigated by several researchers [9-17]. In their publications it has been shown that dielectric properties of polymers and blends in general depend on structure, crystallinity, morphology and the presence of fillers or additives. Ghosh and Chakrabarti [8] studied the effect of corporation of conductive carbon black in EPDM and effect of different crosslinking methods on the conductivity. Malik and Prudhomme [18] used the measurement of dielectric properties as a function of temperature as a way to study the miscibility of polymer blend systems.
The present chapter reports the effect of different type of TPU, blend ratio, compatibilisation and nanoclay addition on the properties of TPU/PP Blends. TPU has got high value of dielectric constant. The main drawback of TPU of the outdoor insulation purpose is the absorption of moisture. Our suggested that, blending with PP decrease the water sorption behavior, which is further reduced upon compatibilisation and nanoclay addition. Therefore blending of TPU with a non-polar polymer such as PP is expected to improve the dielectric performance of PP, by reducing the polarity as well as the moisture uptake.

8.2 Results and discussion

8.2.1 Effect of blend ratio

8.2.1.1 Volume resistivity

Basically, polymers have high value of resistivity, owing to the non-availability of free electrons for conduction. Resistivity studies are important for insulating materials, because the most desirable characteristic of an insulator is its ability to resist the leakage of electrical current. Volume resistivity is numerically equal to the direct current resistance between opposite faces of a one centimeter cube of a material, expressed in ohm centimeters. Figure 8.1 shows the variation of volume resistivity \( \rho_v \) of TPU/PP blends as a function of TPU concentration. Polar polymers have lower resistivity than non-polar polymers due to the polarization of polar polymers under the influence of electrical field, which promote the conducting process.
From the Figure 8.1 it is clear that PP is a good insulator with very high value of volume resistivity where as the volume resistivity of TPU is very low. In the case of blends the volume resistivity values are in between that that of TPU and PP. As the concentration of TPU increases the volume resistivity values decreases.
Figure 8.2. Volume resistivity of ester-TPU, PP and their blends as a function of frequency at 30° C

Figure 8.3. Volume resistivity of ether-TPU, PP and their blends as a function of frequency at 30° C
Volume resistivity of TPU, PP and their blends as a function of frequency is given in the Figure 8.2. It can be seen from the Figure 8.2 that, with incorporation of TPU, which is comparatively a less insulating material, reduces the volume resistivity of the blends. In TPU/PP (30/70) blend where PP forms the matrix, the curve is very close to PP curve and in TPU/PP (70/30) the curve is very close to TPU. In all cases reduction in volume resistivity is observed with increase in frequency. This can be attributed to the increase in molecular mobility at high frequencies.

8.2.1.2 Dielectric constant (\(\varepsilon'\))

The dielectric constant (\(\varepsilon'\)) is an important parameter for an insulating material. It is an expression of the extent to which a material concentrates electric flux. The dielectric material is a substance that is a poor conductor of electricity, but an efficient supporter of electrostatic fields. Materials with high dielectric constants are useful in the manufacture of high value capacitors. The variation of dielectric constants of TPU, PP and their blends as a function of frequency is shown in the Figure 8.4 and 8.5. It is evident from the figure that \(\varepsilon'\) values of pure TPU and their blends decrease with increasing the applied frequency. Generally the dielectric constant of a polymer arises from various polarization phenomena that come into play when the polymer is subjected to an electric field. The dielectric constant increases with increase in polarizability. The different types of polarization possible in a material are (1) electronic polarization (2) atomic polarization and (3) orientation polarization [19]. The orientation polarization contributes a major part of the total polarization for polar polymers. In heterogeneous materials, there is a possibility for interfacial polarization, which arises due to the difference in conductivities of the two phases [20]. Therefore in the case of TPU, which is a polar polymer, all the three
types of polarization contribute towards the dielectric constant. As a result, TPU exhibits high dielectric constant, especially at low frequencies.

**Figure 8.4.** Variation of dielectric constant of ester-TPU/PP blends with frequency at 30° C

**Figure 8.5.** Variation of dielectric constant of ether-TPU/PP blends with frequency at 30° C
The time required for each type of polarization to reach the equilibrium level varies with the nature of polarization. The orientation polarization requires more time compared to electronic and atomic polarization to reach equilibrium value. The interfacial polarization generally occurs at lower frequencies. In the figure high values of dielectric constant in the low frequency region can be attributed to the interfacial polarization effects. But at higher frequency the interfacial polarization is less prominent and hence the dielectric constant is due to the orientation, electronic and atomic polarization. We can explain the effect of high frequency in this way also. Under the influence of an electric field, polar polymers tend to form dipoles, and these dipoles under the influence of an external field, oscillate with the frequency of the field. The effect is more pronounced at high frequency. When the heat build up is more, this results in the deterioration of electrical properties. The orientation of the dipoles depends on the crystallinity of the medium. Since TPU is amorphous, dipoles can orient more easily. Such increase in dielectric constant of polar polymers was reported by various authors [21-23].

PP exhibits having low dielectric constant values characteristic of non-polar materials. The higher the viscosity of the polymer, the greater will be the hindrance to free dipolar orientation polarization from the neighboring molecules, and the lower will be the dielectric constant [24].

In the case of blends, due to the presence of two phases TPU and PP with different conductivities, interfacial polarization occurs leading to an increase in dielectric constant. From the figure it can be seen that the dielectric constant increase with in TPU content at all frequencies. This is due to the increases in the dipoles by the addition of the TPU. Since interfacial polarization decrease with increase in frequency, the dielectric
constant has contribution from orientation, atomic and electronic polarizations at higher frequencies.

PP shows lowest dielectric constant value, which is a characteristic of a non-polar material and TPU shows the highest value. The blends show intermediate values. In the case of blends the values increase as the TPU content increase. The increase with the incorporation of TPU is due to the increase in dipoles, which increase the orientation polarization and also due to the presence of interfacial polarization. The non-linearity of the curves observed in the TPU/PP blend systems is due to the incompatibility of the blends. This type of non-linearity in $\varepsilon'$ values was reported by the Saad and Sabbagh [25-27]. In the case of TPU/PP (30/70), TPU is dispersed with poor bonding with the matrix whereas, in TPU/PP (70/30) TPU is the matrix. Thus relatively high value of $\varepsilon'$ on the addition of TPU can be correlated with the continuous nature of TPU phase leads to a better orientation of dipoles. The dielectric constant depends on resistivity according to equation.

$$\log R_{10} (298\text{K}) = 23-2 \varepsilon' (298\text{K})$$ \hspace{1cm} (8.1)

i.e, the electrical resistance of polymers decreases exponentially with increasing dielectric constant. In TPU/PP blends as the dielectric constant increases with the increase in TPU content, the volume resistivity decreases (Figure 8.1).

8.2.1.3 Dissipation factor and loss factor ($\varepsilon''$)

The tangent of the dielectric phase angle or the tangent of the dielectric loss angle is represented by the tan $\delta$. The measurement of dissipation factor (tan $\delta$) and loss factor ($\varepsilon''$) of an insulating material is important. In electrical applications, it is desirable to keep the electrical
losses to a minimum. Electrical loss indicates the inefficiency of an insulator. The loss tangent is a measure of the alternating current electrical energy, which is converted into heat in an insulator. This heat raises the temperature, leading to deterioration of the polymeric materials. The variation of tan δ and loss factor with frequency for TPU, PP and their blends is depicted in the Figure 8.6 and Figure 8.7 respectively. Addition of TPU into PP increases dissipation and loss factor. The increase in the value is due to orientation polarization of polar TPU followed by oscillation under electric fields.

![Figure 8.6](image)

**Figure 8.6.** Variation of dissipation factor of ester-TPU /PP blends with frequency at 30° C
Figure 8.7. Variation of loss factor of ester-TPU/PP blends with frequency at 30° C

Figure 8.8. Variation of dissipation factor of ether-TPU/PP blends with frequency at 30° C
Figure 8.9. Variation of loss factor of ether-TPU /PP blends with frequency at 30° C

8.2.1.4 Comparison with theory

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

\[ \varepsilon'_{0} = V_1 \varepsilon'_1 + V_2 \varepsilon'_2 (1 - V_1) \]  \hspace{0.5cm} (Model 1) \hspace{1cm} (8.2)

where \( \varepsilon'_1 \) and \( \varepsilon'_2 \) are dielectric constants of components 1 and 2 and \( V_1 \) and \( (1 - V_1) = V_2 \) are the volume fractions of components 1 and 2 respectively. The logarithmic variation of dielectric constant can be expressed by the equation,

\[ \log \varepsilon' = V_1 \log \varepsilon'_1 + (1 - V_1) \log \varepsilon'_2 \]  \hspace{0.5cm} (Model 2) \hspace{1cm} (8.3)

The dielectric constant of two-phase mixtures based on spherical particle, which consider all the possible interaction, could be calculated using the following equation [28]
\[ e'_c = \frac{1}{4} \left( H + \left( H^2 + 8e'_1, e'_2 \right)^{\frac{1}{2}} \right) \]  

(Model 3) \hspace{1cm} (8.4)

where \( H = (3V_1-1) e'_1 + (2-3V_2) e'_2 \) \hspace{1cm} (8.5)

The Maxwell-Wagner-Sillars equation [29] was also used to predict the \( e' \) values and is given as

\[ e'_c = e'_2 \frac{2e'_2 + e'_1 + 2V_1 (e'_1 - e'_2)}{2e'_2 + e'_1 + V_1 (e'_1 - e'_2)} \]  

(Model 4) \hspace{1cm} (8.6)

Experimentally obtained dielectric constants (at a frequency 1 MHz) for the various blend compositions were compared with theoretical models. The comparison is depicted in the Figure 8.10, which shows that experimental values deviate from all the models. The experimental values are much lower than that of various theoretical models, which is attributed to the incompatible nature of the blend. Maximum deviation is shown for the Maxwell-Wagner Sillars equation and model 3.

![Figure 8.10. Comparison of experimental values obtained for dielectric constant with theoretical predictions for ester–TPU based blends](image-url)

The graph shows the comparison between experimental values and theoretical predictions for various models. The experimental values are significantly lower than the theoretical predictions, demonstrating the incompatibility of the blend.
8.2.2 Compatibilised blends

The two polymers TPU and PP are incompatible. The immiscible blends have got unfavorable interactions which lead to unstable morphology and poor interfacial adhesion, which leads to the inferior properties of the blends. These limitations can be overcome by compatibilisation. Hence a reactive route was employed to compatibilise the system using MA-g-PP as the compatibiliser. The urethane group of the TPU can react with the anhydride group of the compatibiliser to form a graft polymer, which can locate at the interface. Analysis of phase morphology, mechanical, DMA and thermal properties proved that MA-g-PP could act as an effective compatibiliser in TPU/PP blend system. In this context we analyzed the effect of compatibilisation on the dielectric properties of 70/30 (TPU/PP) blends. Both ester- and ether- based TPU was used for these studies because soft segment of ester and ether TPU has different surface tension values.
Further, nanoclay was incorporated in the system to reduce the surface tension of TPU hard segment to make the blend more compatible.

8.2.2.1 Volume resistivity

![Figure 8.12](image1)

**Figure 8.12.** Effect of compatibiliser concentration on the volume resistivity as a function of frequency at 30°C for ester based TPU based blends

![Figure 8.13](image2)

**Figure 8.13.** Effect of compatibiliser concentration on the volume resistivity as a function of frequency at 30°C for ether based TPU based blends

The effect of compatibilisation on the volume resistivity of the TPU/PP(70/30) blends is given in the Figure 8.12. It is quite evident from the figure that compatibilisation resulted in the increase of volume resistivity[30-31]. The highest value of volume resistivity is observed at 5% of compatibiliser concentration. With the incorporation of 3 wt% of MA-g-PP, the resistivity becomes almost close to that of the uncompatibilised blends. During the 3% addition of the compatibiliser, the anhydride group will react with the urethane groups of TPU, contributing towards the reduction in
overall polarity of the system. When the concentration of the compatibiliser increases above CMC level, the amount of polar groups in the system increases. This is reflected in the volume resistivity at high compatibiliser loading. The morphology of the compatibilised blends suggests that, by the incorporation of 5 wt% of the compatibiliser, CMC is reached [Figure 3.3(a)]. Therefore, further addition of the compatibiliser will lead to the formation of micelles. It is expected that the micelles aggregates of the compatibiliser will result in the increase of polarity.

8.2.2.2 Dielectric constant

The results of the effect of compatibilisation on the dielectric constant of TPU/PP(70/30) blends are given in Figure 8.16. It can be observed from the figure that compatibilisation resulted in a substantial decrease of dielectric constant. The lowest value of dielectric constant was
observed at 5% of compatibiliser addition. Further addition of the
compatibiliser increased the dielectric constant. As discussed earlier, this
observation may be due to the formation of aggregates of the compatibiliser
beyond CMC.

Figure 8.16. Effect of compatibiliser concentration on the dielectric
constant as a function of frequency at 30°C (a) Ester – TPU
based (b) Ether – TPU (based)

Figure 8.17. Effect of nanoclay addition on the dielectric constant as a
function of frequency at 30°C for compatibilized (a) Ester -
TPU based (b) Ether-TPU based
8.2.2.3 Dissipation factor and loss factor

Figures 8.18 to 8.21 show the variation of dissipation factor (\(\tan\delta\)) and loss factor (\(\epsilon''\)) on compatibilisation. As the frequency increases, \(\tan\delta\) and loss factor decreases and then levels off. The loss factor and dissipation factor reaches a minimum at 5% loading of the compatibiliser. Increase in loss factor and dissipation factor at high concentration of MA-g-PP can be attributed to the increase in the polarity of the systems at high loadings. The lower values of \(\tan\delta\) and \(\epsilon''\) for TPU(nano)/PP/MA-g-PP (compatibiliser loading of 5% , nanoclay loading of 3%) implies that insulating property can be improved by using optimum concentration of the compatibiliser and nanoclay.

**Figure 8.18**
Figure 8.18. Effect of compatibiliser concentration on the dissipation factor as a function of frequency at 30° for ester-TPU based blends

**Figure 8.19**
Figure 8.19. Effect of compatibiliser concentration on the dissipation factor as a function of frequency at 30° for ether-TPU based blends
Figure 8.20. Effect of nanoclay addition on the dissipation factor as a function of frequency at 30°C for compatibilized (a) Ester - TPU based (b) Ether-TPU based

Figure 8.21. Effect of nanoclay addition on the loss factor as a function of frequency at 30°C for compatibilised (a) Ester -TPU based (b) Ether-TPU based
8.3 Conclusion

In this chapter electrical properties of ester- and ether- based TPU, PP and their blends were analysed in the frequency range 1Hz to 1MHz. Compared to polar TPU, PP exhibited good insulating properties. Among the neat polymers, PP possessed the maximum volume resistivity and minimum dielectric constant. The volume resistivity values of the blends fall in between those of TPU and PP. TPU has got high dielectric constant. With the addition of PP, the dielectric constant decreased due to the decrease in the overall polarity of the system. By comparing the experimental dielectric constant values with theoretical models, it was found that Maxwell-Wagner-Sillars equation model 3 deviated maximum from the experimental values.

Compatibilisation increased the volume resistivity. This may be due to the decrease in the polar groups in the system upto CMC level. The lowest value for the dielectric constant was observed at 5% addition of MA-g-PP. The loss factor and dissipation factor reached a minimum at 5% loading of the compatibilisers. Further addition of nanoclay to this system reduced the dissipation factor and loss factor.

8.4 References

1. T. Tokoro, R. Hackam, Loss and recovery of hydrophobicity and surface energy of HTV silicone rubber, IEEE Trans Dielectrics Electrical Insulat 8,1088 (2001)


