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Title: **ELASTOMERIC BLENDS OF NATURAL RUBBER/AILANTHUS MALABARICUM RESIN WITH IMPROVED ELECTRICAL PROPERTIES FOR FLEXIBLE ELECTRONICS**

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## ELASTOMERIC BLENDS OF NATURAL RUBBER/AILANTHUS MALABARICUM RESIN WITH IMPROVED ELECTRICAL PROPERTIES FOR FLEXIBLE ELECTRONICS

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### ABSTRACT

Natural Rubber based composites have been prepared by reinforcing silk fabric. The matrix material for the composite is Glutaraldehyde cured natural rubber. It shows excellent mechanical strength and other physical properties. In the proposed investigation, silk is proposed as reinforcement into the same matrix material. Silk is ecofriendly and biodegradable material with excellent tensile strength. When such kind of fabrics is introduced into the vulcanized rubber as the matrix, it is expected to enhance the physical properties considerably. A considerable enhancement in the stability of natural rubber in terms of tensile properties is noticed on reinforcing fabric into rubber.

### KEYWORDS

Silk, Natural Rubber, Glutaraldehyde, Tensile Properties, Solvent Transport.

### 1. INTRODUCTION

Polymers are widely used in our daily life from the past few decades. There are varieties of polymers which are used in different applications to develop material with desired properties. Blending of two or more polymers is an important technique to design and develop materials with desired physical properties [1-3]. It is an easy method to produce the material for various applications by reducing the production cost. Synthesize a new polymer or monomer increases the cost of production. Instead of synthesizing a polymer, the researchers have been developed blending technique to achieve the material with better property profile that lies between the properties of individual polymers [4, 5]. The combination of properties of two polymers is the advantage of blending technique.

Rubbers can be classified into two types based on

the origin namely natural and synthetic rubbers. Poly isoprene or natural rubber is a high molecular weight polymer. Synthetic rubber cannot be processed easily with any additives. Properties of natural rubber can be improved by adding other polymers and reactive compounds. Dicumyl peroxide vulcanizes natural rubber around 150°C [6]. Crosslinking between rubber molecules opposes the free movement of rubber when the load is applied. It was reported that the resin exudated from Ailanthus Malabaricum tree can be crosslinked with Dicumyl peroxide [7]. As a common crosslinking agent, Dicumyl peroxide crosslinks both the polymers simultaneously.

Effect of crosslinking on the dielectric properties of rubber was investigated by Boggs and Blake [8]. They showed that the dielectric constant of rubber increases with increasing the percentage of crosslinking agent. Further, it reduces due to the

reduction of double bonds of rubber macro molecules. The free rotation of carbon-carbon bond in long chain molecule is responsible for the dielectric loss in crosslinked rubber [9]. Dielectric constant of crosslinked rubber mainly depends on the concentration of crosslinking agent. A new blend system has been introduced to improve the dielectric properties of natural rubber. Blending of highly elastomeric materials improves the elasticity of rubber. Resin exudated from *Ailanthus Malabaricum* tree shows excellent elasticity compared to natural rubber. It consists of many reactive functional groups in its main chain and increases the polarity. Flexible materials such as rubber and its blends are being extensively used in curved circuits and flexible displays. Stretchable thermometers and biomedical devices are designed by using such type of flexible electronic circuits. Materials with mechanically flexible nature are essential for flexible electronic applications. These materials should have optimum relative permittivity and low loss tangent. Elastomers are flexible and show very low relative permittivity. Therefore, such types of materials are unfavorable for practical applications. It is very difficult to get a single-phase material with all the required properties. Blending of excellent elastomers is the most convenient way to obtain the required properties together. The circuits must be flexible and stretchable in case of such type of systems. This paper presents the experimental results of dielectric and ac conductivity studies of natural rubber and resin blends in the frequency range 100 Hz to 8 MHz.

In the present investigation, an attempt has been made to enhance the elastomeric nature and electrical properties of natural rubber by the addition of a resin exudated from *Ailanthus Malabaricum* tree. Resin (ER) exudated from the tree *Ailanthus Malabaricum* is an amorphous aromatic polymer and it is bulkily available in south India. It has been already reported that the resin can be crosslinked by using dicumyl peroxide [7]. Blends were prepared with various compositions and the variation in electrical properties has been studied. Dicumyl peroxide was used as the common crosslinking agent for

both the elastomers.

## **2. MATERIALS AND METHODS**

### **2.1 Materials**

Natural rubber in the form of sheet was purchased from the rubber plantation located at South Karnataka, India. Exudated resin was collected from the *Ailanthus Malabaricum* trees cultivated at the belt of Western Ghats, Karnataka, India. Dicumyl Peroxide and Benzene were supplied by HiMedia Laboratories Pvt. Ltd. Mumbai, India.

### **2.2. Preparation of Blend Samples**

Exudated resin was initially dissolved in benzene at room temperature and filtered the solution to remove the non-polymer contents. The solution was then kept for 5 hours to settle down the polymer part at the bottom of the beaker at room temperature. Then the top portion was removed from the beaker and bottom part kept in oven at 60 °C for 24 hours to evaporate the benzene. The dried sample was used to make the blends. Natural rubber and the elastomeric resin were dissolved in benzene and mixed with suitable blend proportions by using a mechanical stirrer. 2 % (w/w) Dicumyl peroxide (DCP), the cross-linking agent was then accurately weighed and dissolved in benzene. The solution of Dicumyl peroxide was then slowly added to the blend solution and stirred well for 1 hour. Then the same solution was transferred to the Petri dish and kept in oven at 70 °C for 24 hours. These dried blend samples were peeled out and compression molded using hydraulic press at 10 ton maintained at 140 °C for 20 minutes. The film thickness was reduced to 2 to 2.5 mm.

### **2.3 Morphology**

Scanning Electron Microscopy (SEM) with JEOL JSM 5800LV instrument was employed to analyze the surface morphology of the prepared sample. With this method the surface of the sample was exposed to an electron beam and the electrons emission from the sample specimen was detected and amplified to get an image of the sample. The accelerating voltage range and current are 1-40 kV and 20 micro amperes respectively. On a video monitor the resultant image of the sample was often viewed. The resolution achievable ranges down to 2 nm. Since, SEM shows a relatively a larger depth of field,

thus can show typical features better than other microscopic techniques (except atomic force microscopy). A thin layer approximately 10 nm of a conductive metal gold was sputtered onto the surface to make the surface conductive.

## 2.4. X-RD

X-ray diffraction was performed by an X'Pert MPD, Philips X-ray diffractometer under the following conditions: Nickel filtered Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) at a current of 25 mA and a voltage of 35 kV. The scanning rate was 4°/min in the angle range 5–50° (2 $\theta$ ).

## 2.5. Dielectric and ac conductivity studies

Both surfaces of all the samples were coated with silver paste to create a better contact with the electrodes. In addition, the samples were dried overnight in an oven at 40°C under vacuum and then kept in dried environment, for the elimination of any moisture effects. The capacitance and dielectric loss of the blends were measured at frequencies ranging from Hz to MHz at 27 °C using an Impedance Analyzer model N4L PSM1735. The accuracy of the measurement was about  $\pm 0.97\%$ . The dielectric constant was measured from capacitance using the equation,

$$\epsilon' = C t / \epsilon_0 A \quad (1)$$

where C is the capacitance; t, the thickness; A, the area and  $\epsilon_0$ , is  $8.85 \times 10^{-12}$  F/m and

$$\text{Loss factor, } \epsilon'' = \epsilon' \tan \delta \quad (2)$$

The a.c conductivity ( $\sigma_{ac}$ ) values are obtained from the formula,

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \quad (3)$$

The above equation can be rewrite as,

$$\sigma_{ac} = f \epsilon' \tan \delta / 1.8 \times 10^{10} \text{ (S/cm)} \quad (4)$$

where, f is the frequency of measurement.

The dielectric constant and dielectric loss of NR, Resin and its blends have been carried out at different frequencies ranging from  $10^2$  to  $10^6$  Hz.

## 3. RESULTS AND DISCUSSIONS

Surface morphology of the blends is studied by using scanning electron microscopy. The photographs obtained from the scanning electron microscopy of vulcanized rubber and its blends with different elastomer compositions are as shown in Figure 1. Vulcanized rubber exhibits a porous nature as it can be seen in the SEM

microphotographs. The incorporation of both the elastomeric phases reduces the porosity of the constituent polymer phase as seen in figure. With the addition of exudated resin, a better surface morphology can be attained for natural rubber. In the present system one elastomeric phase is interpenetrated into other elastomeric phase by blending. Consequently, the morphology of the blend shows a better non-porous nature. A fine dispersion of elastomeric resin phase in to natural rubber is seen in the blend. In the literature many reports are available to compare the electrical properties with surface morphology of polymer blends [10-12]. The free volume of a polymer has a major role to decide the electrical properties. Dielectric constant and conductivity reduce with increase in the free volume. On incorporating the resin in to rubber reduces the free volume exists in rubber. This is one of the reasons to increase the dielectric constant and ac conductivity on adding resin in to rubber. Hence, it can be concluded that the surface morphology has a strong influence on the electrical behavior of elastomeric blends.

X-ray diffraction is an advanced technique to analyze the structural changes of a polymer blend [13]. The XRD patterns of vulcanized rubber and its blend with exudated resin is shown in Figure 2. A crystalline peak appeared at 20° for vulcanized rubber and its blend with exudated resin. By the incorporation of elastomeric resin phase in the blend the intensity of the crystalline peak reduces. It clearly indicates that, the crystallinity of the blend is reduced by the addition of resin into natural rubber phase. With the high percentage of resin in the blend shows more amorphous. It is observed that there is a reduction in the intensity by cross-linking the blend components. The formation of Cross-links between the polymer molecules may be the reason to reduce the crystallinity in the blends. As a result of cross linking, the width at half height has also been reduced. Dielectric constant of a material is the measure of its ability to polarize when the electric field is applied. Energy can be stored in a dielectric medium by polarizing the material on applying the field. Electronic and atomic polarizations are not considerably taking place in

case of polymeric materials. Orientational or dipolar polarization exists in polymers, such type of polarization occurs in polar polymers from the rotation of side polar groups. Interfacial polarization occurs at the interface of microscopic boundaries in case of polymer blends. The accumulated charges at the boundaries can move through the material on applying the electric field and increases the conductivity. Addition of crosslinking agent increases the strength of elastomeric material. Similarly, dielectric constant and dielectric loss of an elastomer depends on the crosslink density. Bonds generated during crosslinking rotate by applying electric field and it enhances the dielectric properties.

Electrical properties of natural rubber can be modified to certain extent by adding other additives. Incorporation of a polar polymer/elastomer changes the electrical properties of non-polar rubber considerably. Pure rubber is a perfect insulator and shows less dielectric constant. Resin exudated from *Ailanthus Malabaricum* tree consists of many reactive functional groups. It is an oleoresin, the major component is found to be diterpenoids which consists of four isoprene units [14, 15]. Addition of such elastomer in to rubber enhances the functionality of rubber. Table 1 shows the values of dielectric constants at various frequencies for different blend compositions. The values of dielectric constant of natural rubber exhibits the least among the series of blend samples prepared. All types of polarizations are not occurred in cases of non-polar natural rubber, which maintains the minimum value of dielectric constant. Presence of reactive groups such as protein and lipids of natural rubber is the reason to exhibit the minimum value of dielectric constants at various frequencies. There is no much variation in the dielectric constant with frequency in pure natural rubber. Incorporation of resin slowly increases the dielectric constant of rubber. Reactive functional groups present in the resin enhance the dielectric constant of rubber. Resin exhibits the maximum dielectric constant due to the presence of diterpenoids, which has high functionality. Variation of polarization with frequency depends on the time required for each

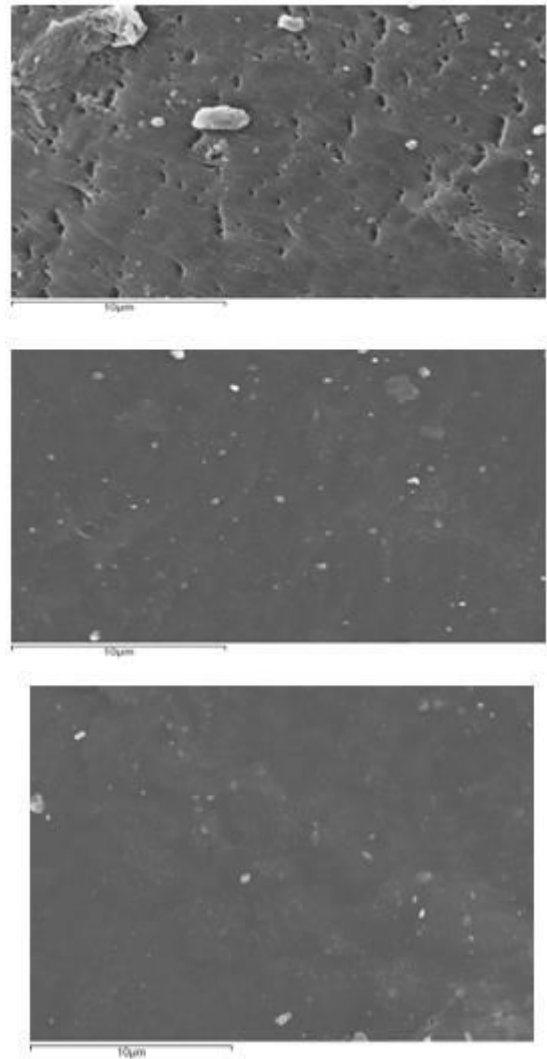
polarization. It changes with the nature of polarization. As a polar material, all types of polarization contribute to increase in dielectric constant. Therefore, resin shows higher dielectric constant at lower frequencies. Interfacial and orientational polarizations vanish with increase in frequency. Both the polarizations need more time to exist within the material. Electronic and atomic polarizations take part at higher frequencies. Therefore, at higher frequency region, dielectric constant of the material arises from electronic and atomic polarizations. Figure 3 shows the variation of dielectric constant with frequency for various blend compositions. A considerable increase in dielectric constant of rubber can be seen in the figure by the addition of resin. Interfacial and orientational polarizations are increased on increasing the percentage of resin in to rubber. Dielectric constant indicates the ability of storing charges in a material. Storage capacity of material can be increased by increasing the value of dielectric constant.

The inability of polarization process in a polymer directly reflects on its dielectric loss when the rate of change of oscillating applied electric field [16]. The time taken for the dipoles to reorient is called relaxation time and it is not an instantaneous process. There will be minimum loss when the relaxation time is comparable with the rate of oscillating electric field. A loss of energy in the heat occurs when the rate of oscillating electric field faster than relaxation time. Relaxation time of interfacial and orientational polarizations is much more compared to the rate of electric field oscillations in polymer blends. Consequently, this leads to a maximum dielectric loss. Dielectric loss of constituent polymers and its blends with frequency are shown in Table 2 and Figure 4. Natural rubber shows the least value of dielectric loss. An increase in dielectric loss is observed on adding resin into natural rubber. The magnitude of dielectric loss reduces with increasing in frequency. Dielectric loss occurs in materials by converting in to heat energy. Dielectric loss is higher at lower frequency region. It arises from the dielectric relaxation of interfacial polarization. More dipoles are incorporated into the system by the addition of resin that leads to a lag in the

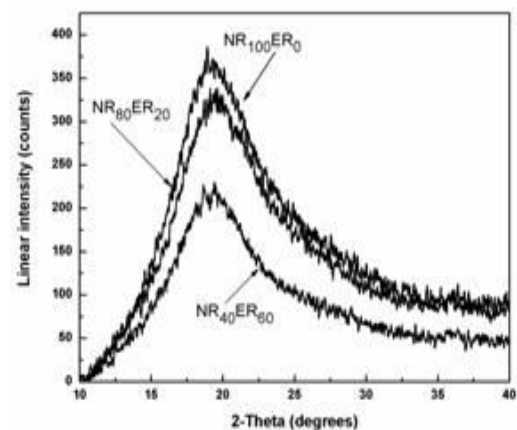
orientation of the dipoles upon the application of electric field. Consequently, an increase in dielectric loss is observed with increase in the amount of resin in the blend. At higher frequency region the dielectric loss remains constant with respect to frequency and blend ratio.

Variation of capacitance for different blend compositions at frequency of 1kHz is depicted in Table 3. Figure 5 shows the effect of blend ratio on the capacitance of natural rubber. An increasing trend can be seen in the figure by the addition of resin. Diterpenoids present in the resin consist of many functional reactive groups develop more number of dipoles in the material, which leads to develop the capacitance of natural rubber. It clearly indicates that, such types of blend materials can be used to fabricate capacitors with various values for desired applications.

AC conductivity of the resulting blend system at 1kHz for various blend compositions is as shown in Table 4. Elastomeric resin exhibits the maximum value of conductivity among the other samples. Increase in conductivity is noticed in the blends on the addition of resin. Increasing the concentration of reactive functional groups may increase the number of dipoles in the blend system. This is attributed to the enhancement in ac conductivity of rubber by the incorporation of resin. Effect of frequency on ac conductivity for various blend compositions is shown in Figure 6. Conductivity study shows an increasing manner with increasing the frequency. At lower frequency region, there is no considerable change in the conductivity for all the samples. Increase in conductivity is observed at higher frequency region. As the frequency decreases, accumulation of charges occurs more at the interfaces. It leads to reduce the number of carriers and conductivity drops at lower frequencies. The mobility of charge carriers is more at higher frequency region and hence conductivity increases. Increase in ac conductivity at higher frequency region can also be related to the electronic polarization and hopping of charge carriers over a small barrier height. Minimum value of conductivity is found for natural rubber and an increasing trend has been observed by the addition of resin into rubber.



**Figure 1.** Scanning electron microphotographs of a) natural rubber, b) blend with 40 % of resin and c) blend with 80 % of resin.



**Figure 2.** XRD patterns of Natural rubber and its blend with ER.

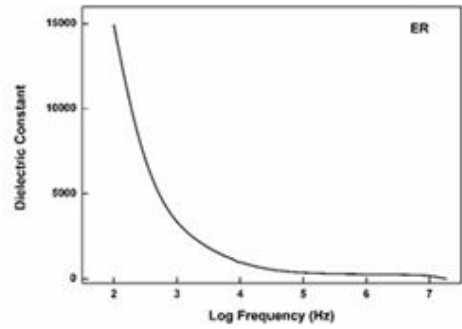
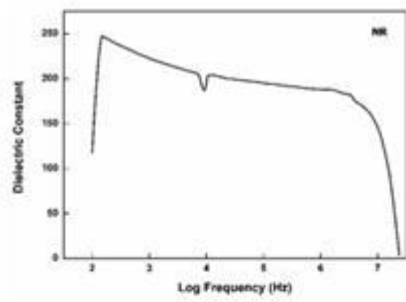
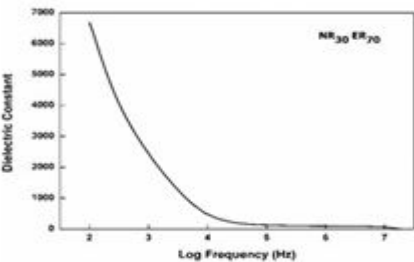
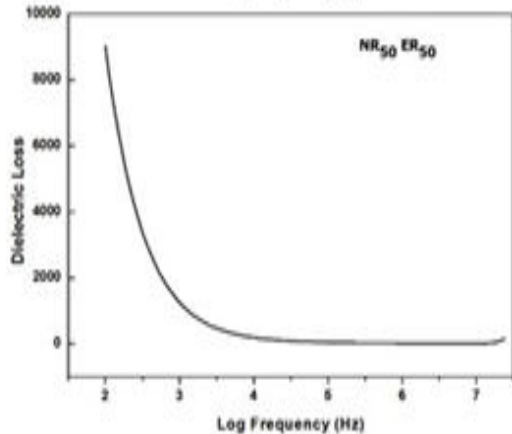
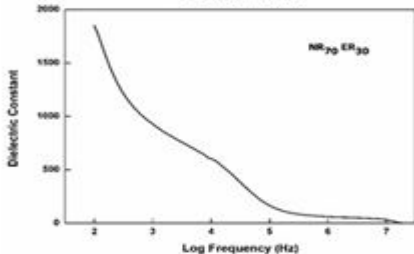
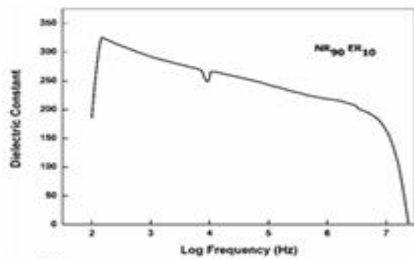
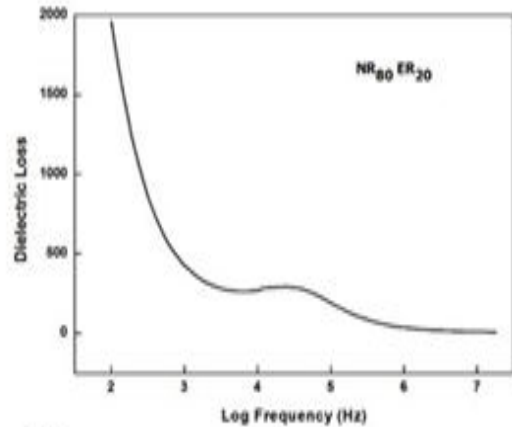
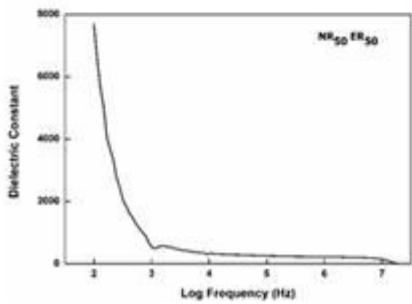
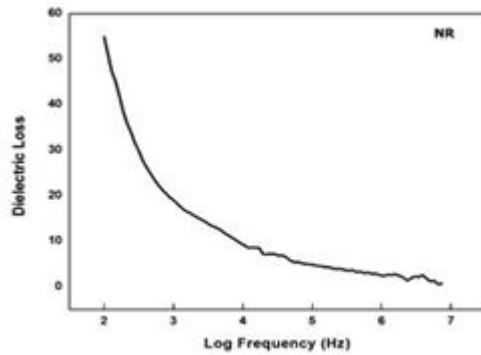
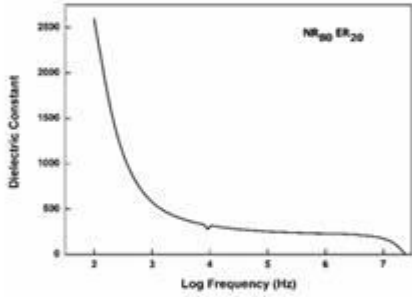


Figure 3. Dielectric constant of NR/ER blends with various compositions.



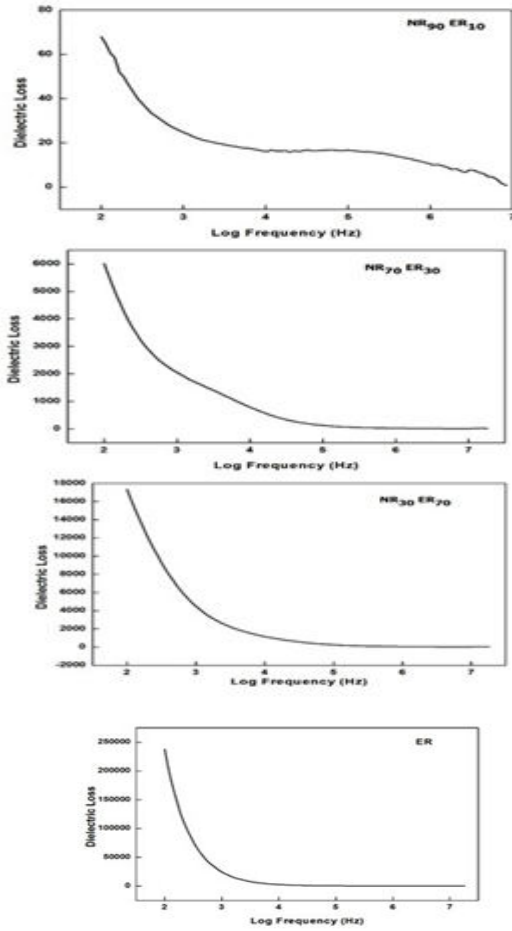


Figure 4. Dielectric loss of NR/ER blends with various compositions

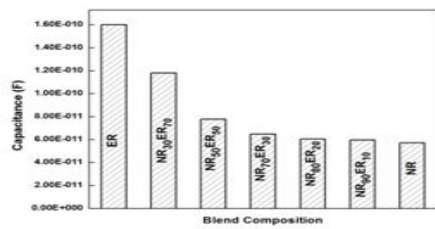


Figure 5. Capacitance of NR/ER blends with various compositions.

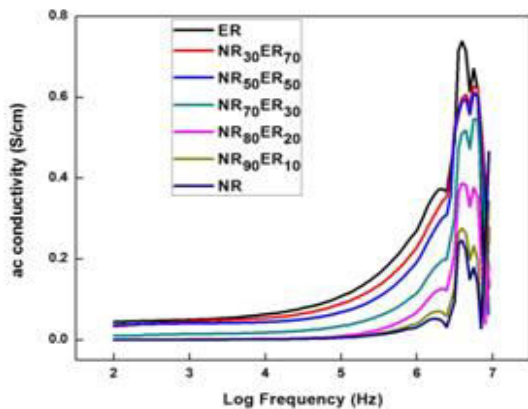


Figure 6. AC conductivity of NR/ER blends with various compositions.

Table 1. Dielectric constant of NR/ER blends for various frequencies.

Sample	Dielectric Constant at Different Frequencies (Hz)									
	5-10 <sup>2</sup>	10 <sup>2</sup>	2-10 <sup>3</sup>	5-10 <sup>3</sup>	10 <sup>3</sup>	2-10 <sup>4</sup>	5-10 <sup>4</sup>	10 <sup>4</sup>	2.5-10 <sup>5</sup>	5-10 <sup>5</sup>
ER	518	311	215	143	98	62	41	24	16	10
NR <sub>90</sub> ER <sub>10</sub>	1423	2428	1722	1028	599	484	284	224	140	102
NR <sub>70</sub> ER <sub>30</sub>	1188	1927	1023	704	487	308	213	151	107	77
NR <sub>50</sub> ER <sub>50</sub>	1087	1713	1118	807	533	362	267	182	131	93
NR <sub>30</sub> ER <sub>70</sub>	1077	1518	1052	761	518	358	251	184	132	95
NR <sub>10</sub> ER <sub>90</sub>	558	351	284	213	147	107	77	51	35	24
NR	211	123	78	58	40	28	20	14	10	7

Table 2. Dielectric loss of NR/ER blends for various frequencies.

Sample	Dielectric Loss at Different Frequencies (Hz)									
	5-10 <sup>2</sup>	10 <sup>2</sup>	2-10 <sup>3</sup>	5-10 <sup>3</sup>	10 <sup>3</sup>	2-10 <sup>4</sup>	5-10 <sup>4</sup>	10 <sup>4</sup>	2.5-10 <sup>5</sup>	5-10 <sup>5</sup>
ER	1076	2463	1217	676	268	121	57	28	14	7
NR <sub>90</sub> ER <sub>10</sub>	729	4427	2087	1088	1137	753	482	279	151	78
NR <sub>70</sub> ER <sub>30</sub>	2733	2848	1852	1179	707	488	311	199	11	10
NR <sub>50</sub> ER <sub>50</sub>	2177	1217	711	197	184	118	62	38	22	17
NR <sub>30</sub> ER <sub>70</sub>	884	424	322	288	139	70	42	27	19	13
NR <sub>10</sub> ER <sub>90</sub>	71	24	20	18	16	16	16	15	15	12
NR	24	18	17	12	9	7	6	4	3	3

Table 3. Values of capacitance of ER/NR blends at 1kHz.

Sample	Capacitance at 1kHz (F)
ER	1.6 × 10 <sup>-10</sup>
NR <sub>30</sub> ER <sub>70</sub>	1.18 × 10 <sup>-10</sup>
NR <sub>50</sub> ER <sub>50</sub>	7.67 × 10 <sup>-11</sup>
NR <sub>70</sub> ER <sub>30</sub>	6.46 × 10 <sup>-11</sup>
NR <sub>80</sub> ER <sub>20</sub>	6.04 × 10 <sup>-11</sup>
NR <sub>90</sub> ER <sub>10</sub>	5.96 × 10 <sup>-11</sup>
NR	5.72 × 10 <sup>-11</sup>

Table 4: ac conductivity of ER/NR blends at 1kHz.

Sample	ac conductivity at 1kHz (S/cm)
ER	0.0495
NR <sub>30</sub> ER <sub>70</sub>	0.0452
NR <sub>50</sub> ER <sub>50</sub>	0.0402
NR <sub>70</sub> ER <sub>30</sub>	0.0139
NR <sub>80</sub> ER <sub>20</sub>	0.00065
NR <sub>90</sub> ER <sub>10</sub>	0.00043
NR	0.00029

## 4. CONCLUSION

Elastomeric blends of natural rubber and resin exudated from Ailanthus Malabaricum tree were successfully prepared by solution casting method. Dicumyl peroxide was employed to crosslink both the elastomeric phases effectively. Effect of blend concentration and frequency response of the blends were studied in detail. An increase in dielectric constant, dielectric loss, capacitance, and ac conductivity was observed in rubber by the addition of exudated resin. More number of reactive functional groups present in the resin enhances the dielectric behavior of natural rubber. By the incorporation of resin phase into natural rubber reduces the porosity of rubber. A better surface morphology is attained for the blend with



higher percentage of exudated resin in the blend. The amorphous nature of natural rubber was also increased by the addition of resin. Based on these studies, it is found that the preparation of this elastomeric blend is beneficial for the development of cost-effective elastomeric materials for specific electric applications.

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