

Studies of Electrical and Mechanical Properties of Semiconductive Poly(vinyl chloride) Compositions

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ABSTRACT: A sample of poly(vinyl chloride) (PVC) and a polar plasticizer consisting of dioctylphthalate (DOP) and triisopropylphenylphosphate (TIPPP) was prepared and found to possess some electrical conductivity. Different samples of PVC compositions were formulated from the PVC-DOP-TIPPP system and also variable proportions of the conductive materials polyaniline or the Ni salt of ethylene glycol bisadipate ester. Dibutyltindilaurate as a heat stabilizer, titanium oxide as a filler, and sandorin red 20 pigment were added. The effect of the structure of polyaniline and Ni adipate ester on the electrical and mechanical properties of the PVC-DOP-TIPPP system was studied to obtain a semiconductive plasticized PVC with good mechanical properties. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 685–693, 1998

Key words: poly(vinyl chloride); electrical and mechanical properties

INTRODUCTION

Polymers in their pure state are excellent electrical insulators ($<10^{-12} \Omega^{-1} \text{cm}^{-1}$), but they can be modified to be relatively good electrical conductors ($>10^{-1} \Omega^{-1} \text{cm}^{-1}$). Conductive polymers offer many advantages compared to classic materials (metals, wood, etc.) such as facilities of processing, low density compared to metals, preservation from corrosion, low hardness, and varied mechanical properties.

Electrical conductivity in polymers can be provided by incorporation of conductive materials such as metals, metal oxides, and metal salts. Naturally, the introduction of metallic materials allows them to envisage the elaboration of polymers possessing the conductive properties of metals and the varied properties of polymers. The addition of a suitable type and concentration of

carbon black (conducting material) to polymers also produces compounds with different degrees of conductivity. Polymers such as polyaniline, polythiophene, and polypyrrole have attracted considerable attention because of their high electrical conductivity. For example, conducting polythiophene and polypyrrole blends with polystyrene were prepared and studied by Fernandez et al.¹ Moreover, Seanor² found that when polystyrene is nitrated or sulfonated, its conductivity rises from 10^{-19} to $10^{-5} \Omega^{-1} \text{cm}^{-1}$.

Conjugated polymers have also been studied with the idea that π electrons that are delocalized along the chains of these polymers could give conductive properties to these systems similar to those of semiconductors. The first conductive polymer was thus realized³ after the success of the doping of polyacetylene. Since this discovery, many conductive polymers have been developed from several monomers that produce conjugated systems after polymerization. Conductive polymers are mainly synthesized by chemical or electrochemical oxidation of monomers in solutions containing a supporting electrolyte.

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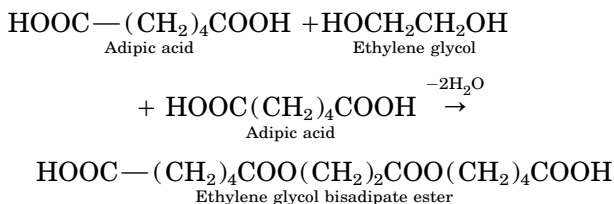
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The aim of this study was to systematically investigate the effect of adding increasing quantities of polyaniline or the Ni salt of ethylene glycol bisadipate ester on the electrical and mechanical properties of a plasticized poly(vinyl chloride) (PVC) in an attempt to improve these properties and obtain a good electrical conducting sample for electronic and microwave device fabrications and battery electrode applications.

EXPERIMENTAL

Preparation of Ethylene Glycol Bisadipate Ester

Ethylene glycol bisadipate ester was synthesized by reacting adipic acid (2 mol) with ethylene glycol (1 mol) in the presence of 1% Al(OH)₃ as the catalyst. The reaction mixture was refluxed for 7 h with vigorous stirring at 210°C. At the end of the esterification process, the product was purified by benzene and dried to produce the ethylene glycol bisadipate ester. The reaction can be illustrated in the following scheme:



The structure of the ethylene glycol bisadipate ester was confirmed by elemental analysis and molecular weight (MW) determination.

Elemental Analysis

	Theoretical (%)	Found (%)
C	52.83	53.46
H	6.92	7.22

The average MW was determined by using the vapor pressure osmometer (VPO) method. The equipment was a Corona Co. VPO (model VPO-117, Japan). The number average MW was found to be 520, which indicates that the structure of ethylene glycol bisadipate ester (calc MW, = 318) is



where $n = 1.64$.

Preparation of Ni Salt of Ethylene Glycol Bisadipate Ester

Ethylene glycol bisadipate ester (10 g) was mixed with a concentrated solution of sodium carbonate. A concentrated solution of nickel sulfate was then added to the mixture that was maintained for 24 h until a precipitate was formed. The precipitate was then purified by washing (3 times in water, benzene, and ethyl alcohol) and dried to produce the Ni salt of ethylene glycol bisadipate ester. The IR spectrum of the Ni adipate ester, measured by an FTIR spectrometer at wave numbers from 4000 to 500 cm⁻¹ and transmittance from 20 to 80% (Fig. 1), shows two peaks at 1705 and 1740 cm⁻¹ that correspond to COOH and COO⁻ groups, respectively, indicating that only partial replacement of the H by Ni in the two carboxylic groups of the ethylene glycol bisadipate ester occurred. This was confirmed by the presence of a high population of free hydroxyl groups as shown from the absorption peak in the 3400–3350 cm⁻¹ region.

Formulations of Samples

In the present study, several formulations were obtained by mixing the components in the proportions shown in Table I. The general procedure for the formulation is described as follows. Homogeneous samples were prepared by adding variable proportions of the prepared Ni salt of ethylene glycol bisadipate ester or polyaniline (average MW 600,000, highly soluble in organic solvents, and has good thermal stability) portionwise at room temperature to a composition containing PVC (K value 70, apparent bulk density 0.3 g/mL, and viscosity number 125 mL/g) and a mixture of dioctylphthalate (DOP) and triisopropylphenylphosphate (TIPPP; Refox 95) plasticizers under stirring. The mixtures were then mixed with dibutyltindilaurate as a heat stabilizer, followed by the addition of TiO₂ as a filler and sandorin red 20 pigment to give the required samples (gelation temperature at 175°C for 100 s). The obtained samples are denoted by $C_0, C_1, C_2, \dots, C_8$. These formulations are shown in Table I.

Mechanical Measurements

Tensile strength and ultimate elongation were determined on an Instron testing machine (model 1026) at 23 ± 2°C with a crosshead speed of 100 mm/min and a load cell range of 0.500 N full scale according to ASTM D 638.77a.⁴ The dimensions

Table II Mechanical Properties of Prepared Samples

	Sample Notation								
	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
Tensile strength (N/cm ²)	255	226	300	155	125	132	94	77	69
Elongation (%)	235	203	305	205	59	158	119	85	55

Schwarz (Germany). The electrical conductivity is calculated using the equation

$$\sigma = \frac{dI}{AV} \text{ mho m}^{-1}$$

where d is the thickness of the sample in meters and A is its surface area in square meters.

RESULTS AND DISCUSSION

Polymers such as PVC are known to have kinetically rigid chains. On the addition of low molecular admixtures, particularly polar plasticizers such as DOP, they are effective enough to penetrate inside the molecular bundles of PVC and to separate the polymeric chains. Accordingly, the mutual interaction between plasticizer and PVC becomes appreciable, leading to aggregates or segments having sizes smaller than that of PVC (i.e., segments of higher molecular mobility). Because the appearance of dipole segments and dipole groups in polymers is associated with the mobility of the kinetic units of the macromolecular chain, the PVC-DOP system should exhibit higher mobilities.⁵

Electrical Properties

In this investigation, the treatment of PVC with a polar plasticizer consisting of DOP and TIPPP produced a PVC-DOP-TIPPP system (sample C_0) that was found to have some electrical properties. In an attempt to improve the electrical properties of sample C_0 and make it into a good electrical semiconductor, polyaniline or the Ni salt of ethylene glycol bisadipate ester were formulated together in different concentrations (Table I). The permittivity (ϵ') and dielectric loss (ϵ'') for the prepared samples ($C_0, C_1, C_2, \dots, C_8$) were studied over the frequency region from 100 Hz to 100 kHz at different temperatures from 20 to 40°C.

It is evident from Figure 2, which represents the variation of ϵ' with frequency at different temperatures, that the value of ϵ' increases with increasing temperature and decreases with increasing frequency. Similar behavior was noted before in the literature.^{6,7} The increase of ϵ' with temperature can be explained by the increase in the mobility of polar groups, a decrease in density, and, hence, a decrease in the effect of the environment that facilitates the orientation of the mobile groups. The decrease of ϵ' with frequency shows an anomalous dispersion. Moreover, Figure 2, as well as Figure 3, which represents the relation between ϵ' and the content of the investigated additives at frequencies of 100 Hz and 100 kHz, show that the value of ϵ' decreases with an increase in polyaniline content and decreases to a greater extent with the increase in the content of Ni salt of ethylene glycol bisadipate ester, especially at the very low frequency region. This could be attributed to steric hindrance due to the presence of large radicals in these additives despite the presence of a number of polar groups that are capable of orientation in an electric field. This restricts the rotation of the large molecules; accordingly, the value of ϵ' decreases.

It is apparent from Figures 4 and 5, which represent the variation of ϵ'' with frequency at different temperatures, that the value of ϵ'' is greatly increased at higher temperatures, especially in the lower frequency region. Moreover, Figures 4 and 5 reveal that, at each temperature, ϵ'' in the lower frequency region increases with increasing polyaniline content and increases to a greater extent with the increase in the content of Ni salt of ethylene glycol bisadipate ester; it is also slightly changed at frequencies after 10 kHz, where it becomes approximately the same for all samples and reaches very small values. This increase in the value of ϵ'' is the result of the high electrical conductivity of these samples in the same sequence.

The low frequency losses may be due to either direct current (dc) conductivity^{8,9} resulting from the increase of ion mobility or the Maxwell–

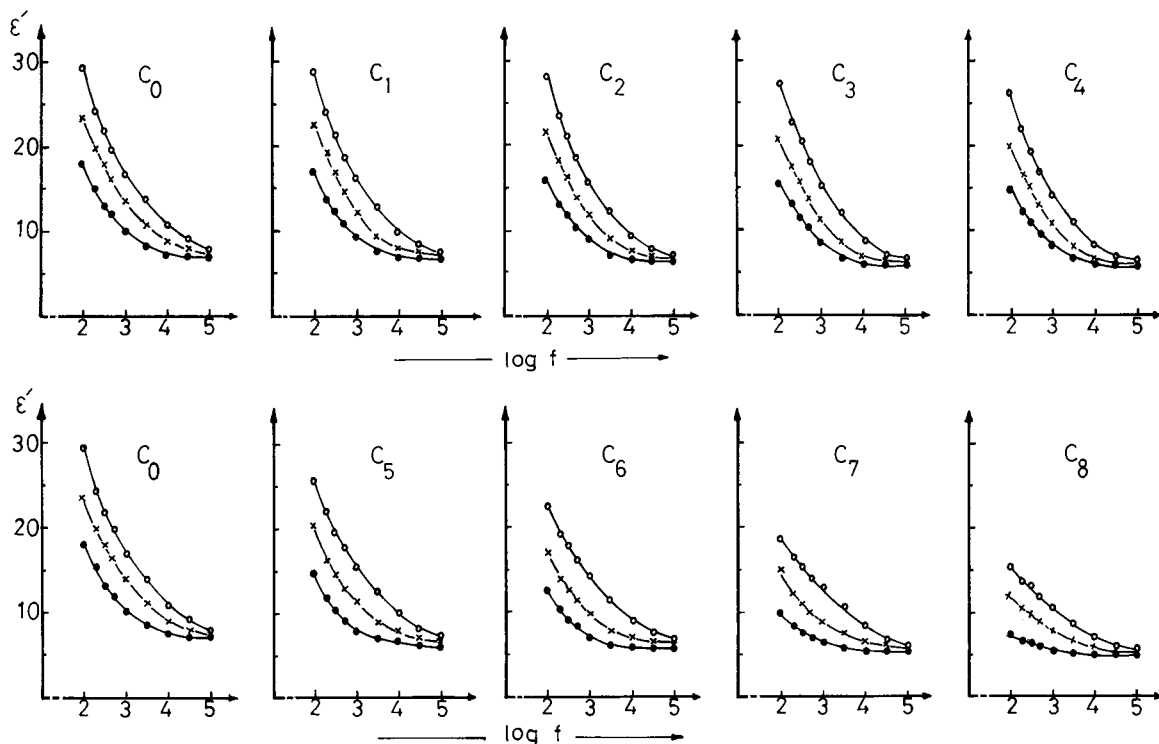


Figure 2 The permittivity (ϵ') versus frequency at (●) 20, (×) 30, and (○) 40°C for the PVC–DOP–TIPPP system mixed with variable proportions of polyaniline and Ni salt of ethylene glycol bisadipate ester ($C_0, C_1, C_2, \dots, C_8$); see Table I.

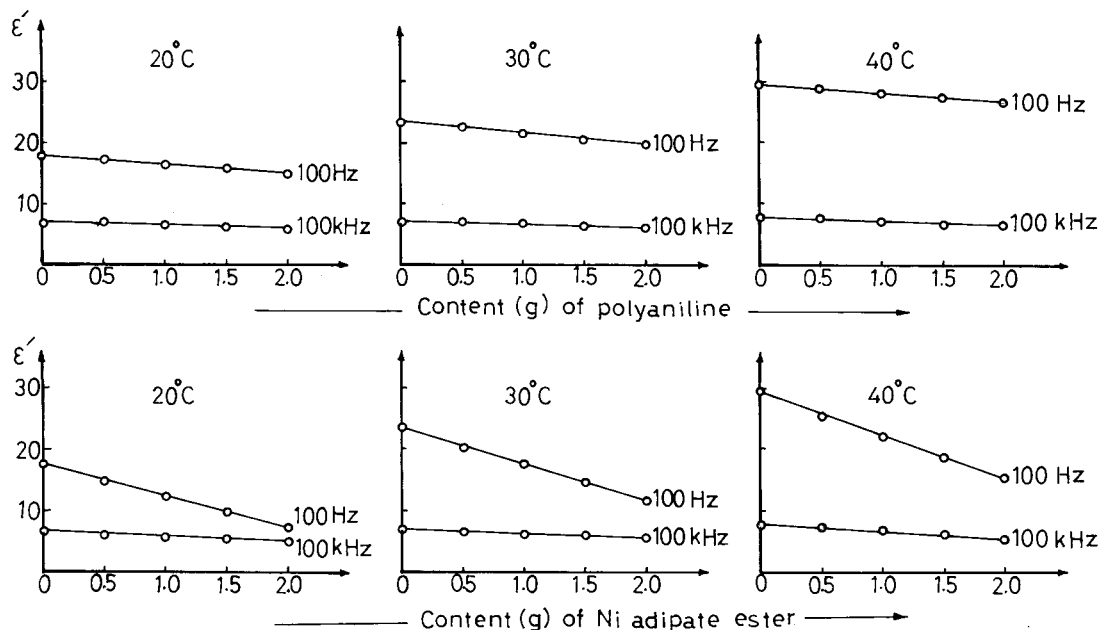


Figure 3 The relation between permittivity (ϵ') and the content of polyaniline or Ni salt of ethylene glycol bisadipate ester at frequencies of 100 Hz and 100 kHz for temperatures of 20, 30, and 40°C.

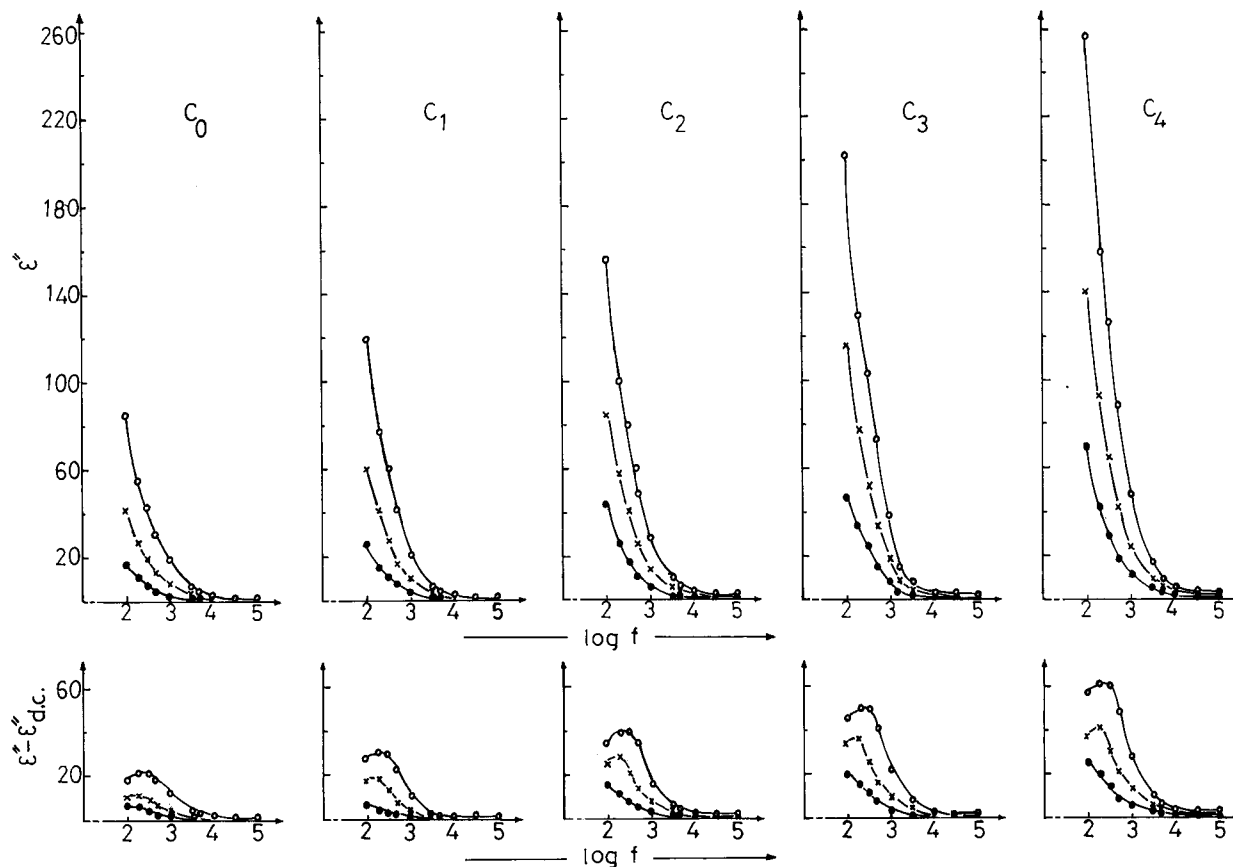


Figure 4 The dielectric loss (ϵ'') and $\epsilon'' - \epsilon''_{dc}$ versus frequency at (●) 20, (×) 30, and (○) 40°C for the PVC–DOP–TIPPP system mixed with variable proportions of polyaniline (C_0 , C_1 , C_2 , C_3 , and C_4); see Table I.

Wagner effect¹⁰ as a result of an alternating current (ac) in phase with the applied potential, or to both. To confirm this, the dc conductivities of the investigated samples were measured by application of Ohm's law to the dc flowing through the samples at 200 V and at temperatures from 20 to 50°C. All investigated samples showed appreciable dc conductivity. The dielectric losses due to the dc conductivity (σ) at the different frequencies (ω) are calculated using the equation¹¹

$$\epsilon''_{dc} = \frac{9 \times 10^{11} 4\pi\sigma}{\omega}$$

and subtracted from the values of ϵ'' in the low frequency region. The data of ϵ'' after subtracting ϵ''_{dc} are plotted versus $\log f$ and represented in Figures 4 and 5. From these figures it is clear that at 20°C for all samples there is an absorption region extending below 100 Hz that may be due to rotation of large aggregates of the chain. Unfor-

tunately, we cannot give further interpretation of this region because we have no measurements below 100 Hz. As the temperature increases, the maximum loss peak increases and becomes clear and is shifted to higher frequency. The increase in the maximum loss peak is also noticed with the increase of the concentration of polyaniline or Ni salt of ethylene glycol bisadipate ester. It is clear from Figures 4 and 5 that the maximum loss peak is higher for sample C_0 mixed with polyaniline than the Ni salt of ethylene glycol bisadipate ester as could be expected from the higher values of ϵ''_{dc} for sample C_0 mixed with the Ni adipate ester.

It may be concluded that the low frequency losses are not totally dc losses and that they may comprise Maxwell–Wagner losses because the differences between the permittivities of the different ingredients in the investigated samples are relatively large.

On the other hand, the change of the electrical conductivity (σ) of samples C_0 , C_1 , C_2 , C_3 , . . . ,

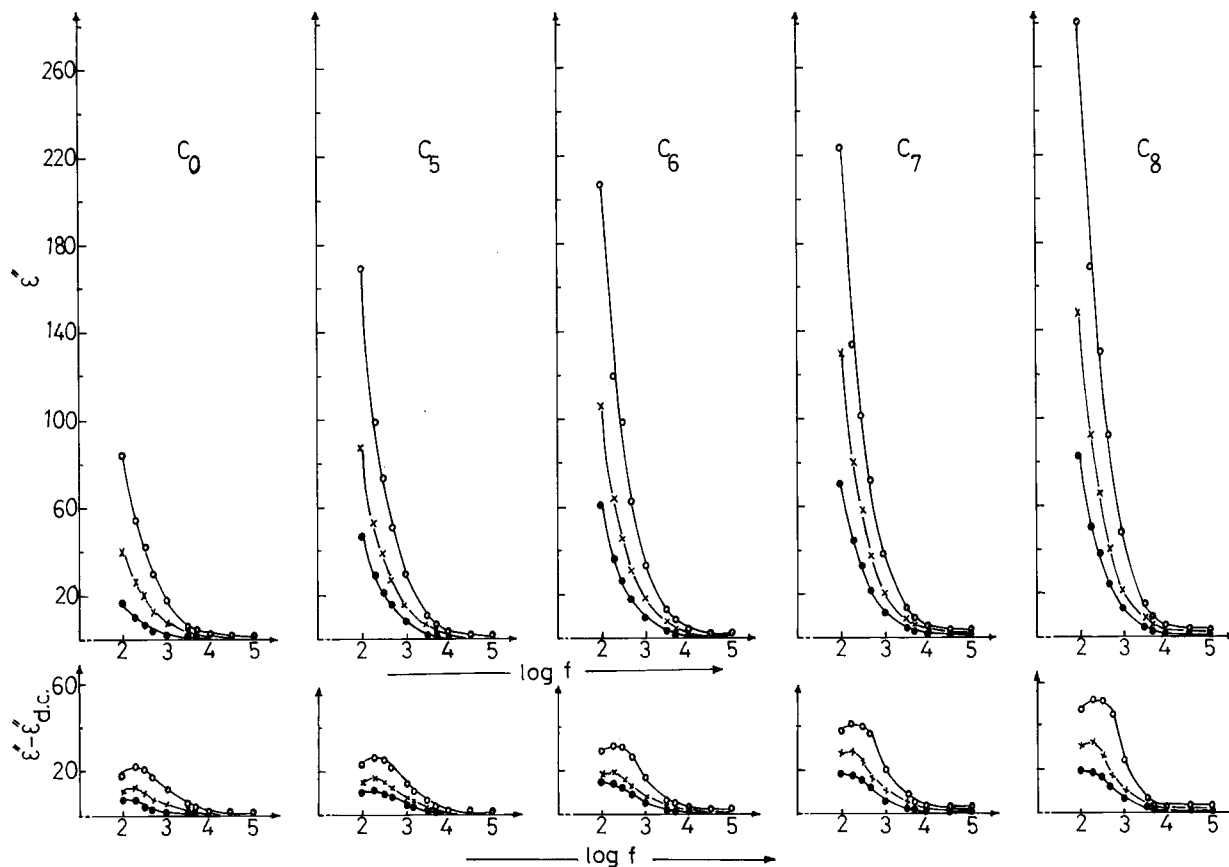


Figure 5 The dielectric loss (ϵ'') and $\epsilon'' - \epsilon''_{dc}$ versus frequency at (●) 20, (×) 30, and (○) 40°C for the PVC-DOP-TIPPP system mixed with variable proportions of Ni salt of ethylene glycol bisadipate ester (C_0 , C_5 , C_6 , C_7 , and C_8); see Table I.

C_8 with temperature is shown in Figure 6. It is evident from this figure that at lower temperatures the σ of these samples was low and increased as the temperature was increased. This may have been due to the increase of the mobility of the ionic bodies that took place as a result of the excitation by heat, leading to an increase in the conductivity of the investigated samples. With respect to sample C_0 mixed with polyaniline (samples C_1 , C_2 , C_3 , and C_4) or the Ni salt of ethylene glycol bisadipate ester (C_5 , C_6 , C_7 , and C_8), Figure 6 also shows that the value of σ increased with the increase in polyaniline content and increased to a greater extent with an increase of the content of Ni salt of ethylene glycol bisadipate ester, especially at higher temperatures. The increase in the value of σ with the increasing content of polyaniline may be attributed to the presence of two unshared electrons on the nitrogen atom of the amino groups in polyaniline that are mobile under the influence of an electric field; thus, it greatly increased the degree of electrical

conductivity in these samples, despite the steric hindrance, due to the presence of phenyl rings incorporated into the polymer backbone as repeat units of aniline that played an important role in decreasing the mobility of the electric charges. Also, the increase in the value of σ with the increased content of Ni salt of ethylene glycol bisadipate ester may have been due to the high electrical conductivity of Ni ions, as well as the presence of a number of polar groups in the Ni adipate ester that are capable of orientation in an electric field. It is significant that the presence of large radicals in the Ni adipate ester may have caused some steric hindrance that partially contributed to decreasing the mobility of the electric charges and, accordingly, the conductivity of these samples decreased to some extent so that the measured conductivity became lower than the expected value when sample C_0 was mixed with Ni ions. Figure 7 shows the relation between conductivity (σ) and the content of polyaniline or Ni adipate ester at temperatures from 20 to 50°C.

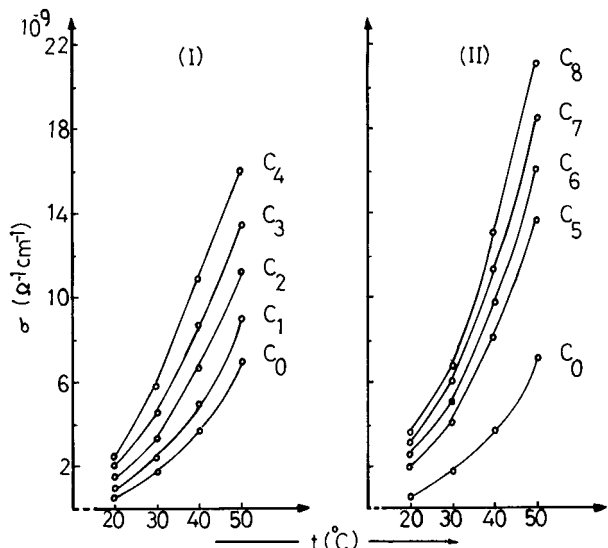


Figure 6 The relation between conductivity (σ) and temperature (t) for (I) samples $C_0, C_1, C_2, C_3,$ and C_4 and (II) samples $C_0, C_5, C_6, C_7,$ and C_8 .

Mechanical Properties

The variation of tensile strength and ultimate elongation versus the concentration of polyaniline or Ni salt of ethylene glycol bisadipate ester at $23 \pm 2^\circ\text{C}$ is given in Table II and is represented graphically in Figures 8 and 9. Figure 8(a) shows that increasing the polyaniline content to 20 g increased the tensile strength from 255 to 300 N/

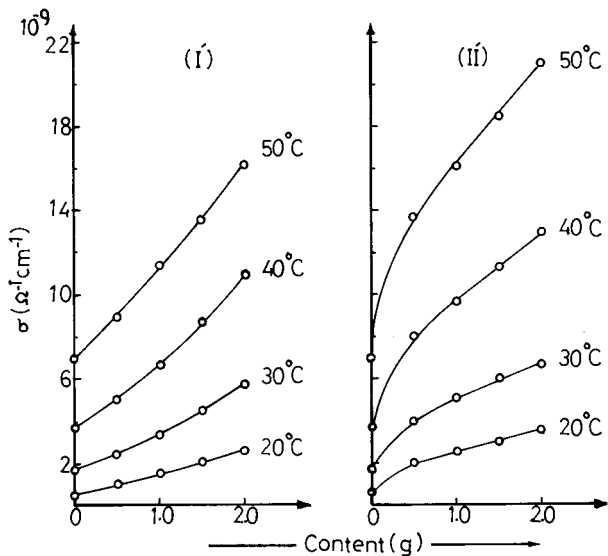


Figure 7 The relation between conductivity (σ) and the content of (I') polyaniline or (II') Ni salt of ethylene glycol bisadipate ester at temperatures from 20 to 50°C .

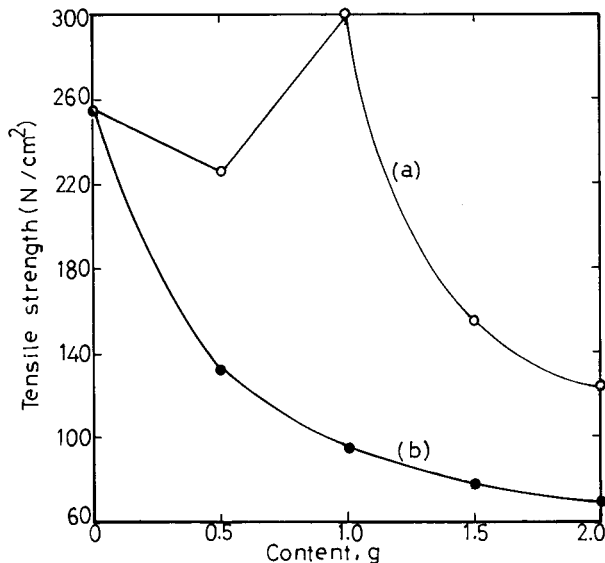


Figure 8 The variation of tensile strength with the content of (a) polyaniline or (b) Ni salt of ethylene glycol bisadipate ester.

cm^2 and then it decreased with a further increase in polyaniline content to 40 g. From Figure 8(b) it is also evident that the tensile strength decreased with the increase of the concentration of Ni salt of ethylene glycol bisadipate ester. This decrease of tensile strength may be explained on the basis that the increase of the concentration of polyani-

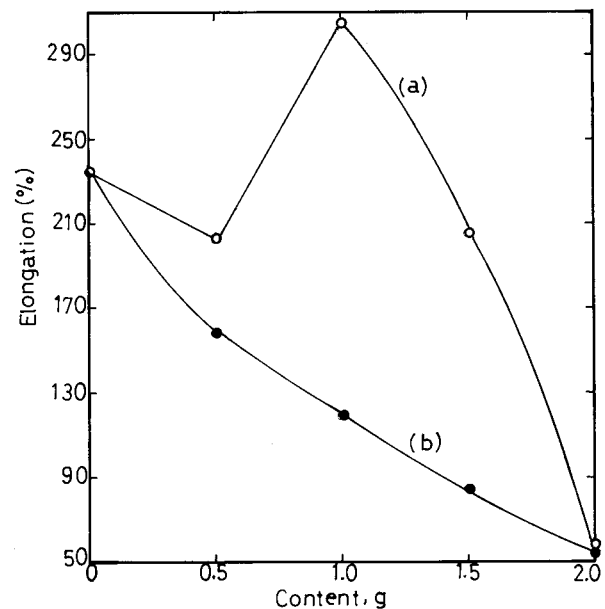


Figure 9 The variation of ultimate elongation with the content of (a) polyaniline or (b) Ni salt of ethylene glycol bisadipate ester.

line or Ni adipate ester caused an increase in the free volume of PVC and facilitated internal molecular movement.¹² On the other hand, Figure 9(a) shows that the ultimate elongation increased from 235 to 305% with increasing the polyaniline content to 20 g and then decreased slowly at higher polyaniline concentrations. So probably intermolecular and interstructural processes may have been present. At low concentrations the intermolecular process was predominant where the polyaniline molecules interacted with the active group of the PVC, leading to the breakage of molecular bundles (aggregates), and the chains were separated. At a polyaniline concentration higher than 20 g, the interstructural process was more prevalent, where the polyaniline molecules were distributed in the interaggregate space. In the first process, elongation increased with concentration whereas in the second process elongation decreased with the increase of polyaniline concentration. Figure 9(b) also shows a sharp decrease in elongation with the increasing concentration of Ni salt of ethylene glycol bisadipate ester.

CONCLUSIONS

It could be concluded that the electrical conductivity of a prepared sample having 100 parts PVC, 60 parts DOP, and 60 parts TIPPP is increased by the addition of polyaniline and increases to a greater extent by adding the Ni salt of ethylene glycol bisadipate ester, especially at the lower frequency region. At the same time, the mechanical properties (tensile strength and ultimate elongation) are decreased with the increase of the concentration of polyaniline or Ni adipate ester up to 40 parts. Therefore, plasticized PVC formulated with 40 parts of Ni salt of ethylene glycol bisadi-

pate ester (sample C₈) possesses the highest electrical conductivity, the best ultimate elongation, and good tensile strength, making it of great interest in the fabrication of electronic and microwave devices and battery electrode applications.

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