Studies of Electrical Properties of Some Fire-Retarding Poly(vinyl chloride) Compositions

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ABSTRACT: Several fire-resistant formulations were prepared from a sample of poly(vinyl chloride) (PVC), small variable proportions of chloroorganic adducts [1,2,3,4,7,7-hexachloro-5-carboxy,bicyclo(2,2,1)heptene-2] or [1,2,3,4,7,7-hexachloro-5-carboxy,5-methyl-bicyclo(2,2,1)heptene-2] as fire-retarding modifiers, plasticizers (dibutylphthalate and a chlorinated paraffin), and a heat stabilizer (dibutyltindilaurate). The fire-resistance and electrical properties of the obtained formulations were studied to obtain a fire-retarding plasticized PVC of good electrical insulation character. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 27–35, 1997

Key words: fire resistance; fire-retarding compositions; poly(vinyl chloride)

INTRODUCTION

Many ways to decrease the flammability of polymers and coatings have been discovered as a result of research done on various mechanisms of flame retardation. Currently, the most effective flame-retardant materials contain halogens, halogenated polycyclic acids, and their derivatives,[1] phosphorus, hydrated alumina,[2] various transition-metal oxides,[3,4] strong acids, or some amine and metal salts.[5] These materials can be used to produce acceptable flame retardance in coatings, when they are either chemically combined with the film-forming polymers or used as additives. Flame-retardant polymers are now emerging as a specific class of materials leading to new and diverse fields of scientific and technological ventures.[6]

Flammability can be reduced by quenching the chain reactions in the flame via addition of free-radical scavengers.[2] Halogen compounds occupy an important position among the fire-extinguishing and flame-retarder agents. The efficiency of these compounds is relatively high.[7]

In this investigation, adducts produced from the diene synthesis using halogenated dienes such as hexachlorocyclopentadiene and dienophils such as acrylic acid or methacrylic acid are used as flame-retarding modifiers for plasticized poly(vinyl chloride)(PVC). The aim of this study was to investigate systematically the effect of adding increasing quantities of these modifiers on the electrical properties of the plasticized PVC to obtain a good electrical insulating sample for wire covering to suit low voltage.

EXPERIMENTAL

Materials

1. Poly(vinyl chloride) (PVC): k value, 70; apparent bulk density, 0.30 g/mL; viscosity number, 125 g/mL.
2. Dibutylphthalate (DBP): specific gravity

20/20°C, 1.045–1.051; n_D^{25}, 1.48–1.49; MW, 278.

3. Chlorinated paraffin: density at 25°C, 1.16–1.18 g/mL; average MW; 366; viscosity at 25°C, 150–350 cp; n_D^{25}, 1.4950 (Cl, 42–45%).

4. Diene: h e x a c h l o r o c y c l o p e n t a d i e n e (HClCPD), bp, 239°C; density at 25°C, 1.717 g/mL; MW, 273; viscosity at 38°C, 5.04 cp; n_D^{25}, 1.5626 (78% Cl).

5. Dienophiles: acrylic acid—bp, 139°C; density at 20°C, 1.051 g/mL; MW, 72.06; n_D^{25}, 1.4202. Methacrylic acid—bp, 163°C; density at 20°C, 1.015 g/mL; MW, 86.09; n_D^{25}, 1.4310.

6. Adducts: 1,2,3,4,7,7-hexachloro-5-carboxy, bicyclo(2,2,1)heptene-2 (adduct A)—bp, 125–127°C/23 mm Hg. 1,2,3,4,7,7-hexachloro-5-carboxy,5-methylbicyclo(2,2,1) heptene-2 (adduct B)—bp, 115–118°C/ 20–22 mm Hg.

Synthesis of 1,2,3,4,7,7-Hexachloro-5-carboxy,bicyclo(2,2,1)heptene-2 (Adduct A)

Adduct A
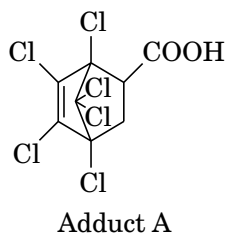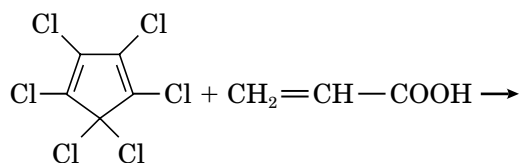
(HClCPD, 0.050 mol, was mixed with 0.025 mol of acrylic acid in a test tube. The tube was firmly sealed and placed in a thermostated electrically heated oil bath for a constant reaction time of 6 h at a reaction temperature of 70°C. No catalyst or solvent was used. The tube was then removed from the oil bath, cooled, and opened. The unreacted diene and dienophile as well as the adduct were separated from the reaction mixture by a careful fractional distillation. This was carried out under atmospheric pressure for the separation of unreacted diene and dienophile and under a subatmospheric pressure of 23 mmHg for the

separation of the adduct at 125–127°C. The adduct was then purified by recrystallization from methylene chloride.

The proposed structure of the new pure adduct was confirmed by

1. Elemental analysis:

	Theoretical (%)	Found (%)
C	27.80	26.70
H	1.15	0.93
Cl	61.73	61.04
O	9.32	8.98

2. IR: The IR measurement was carried out using an FTIR spectrometer at a wavelength 4000–500 cm^{-1} and a transmittance percent from 0–10 [Fig. 1(a)].

3. NMR: A proton NMR spectra deuterio CH$_3$Cl solution containing tetramethylsilane as an internal standard were recorded on Avarian XL-GEM 200-MHz instrument with a chemical shift (D) and expressed in ppm [Fig. 2(a)].

4. Molecular weight determination: The average MW was determined using a CRYETTE A instrument, an automatic cryoscope. The method is based on the Avogadro–Gerhardt Law[8] (Table I).

Synthesis of 1,2,3,4,7,7-Hexachloro-5-carboxy,5-methylbicyclo(2,2,1)heptene-2 (Adduct B)
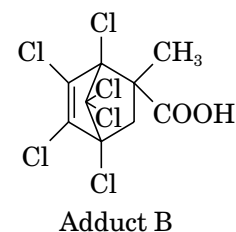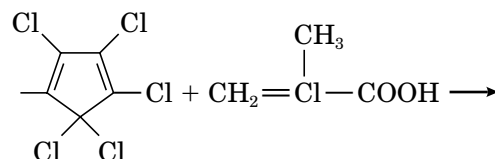
Adduct B

The procedure of the synthesis of adduct B was essentially the same as previously described for the synthesis of adduct A. In this respect, the reaction temperature was 90°C and the separation of

the adduct was carried out under a subatmospheric pressure of 20–22 mmHg at 115–118°C.

The structure of the new pure adduct was confirmed by elemental analysis, IR [Fig. 1(b)], NMR [Fig. 2(b)], and average molecular weight determination as shown before.

Elemental Analysis

	Theoretical (%)	Found (%)
C	30.08	29.3
H	1.67	1.60
Cl	59.33	58.90
O	8.92	8.46

Formulations of the Samples

The materials used in these formulations are fire-retarding modifiers such as adduct A (Cl, 60.8%) or adduct B (Cl, 58.4%) and a preparation containing PVC; plasticizers (DBP and a chlorinated paraffin); and a heat stabilizer (dibutyltindilaurate). The general procedure for formulation is described as follows: Variable proportions of adduct A or adduct B were added portionwise at room temperature to the preparation containing 5 g PVC, 2 g DBP, and 1 g chlorinated paraffin while stirring. Dibutyltindilaurate (0.1 g) was then added and stirring was stopped when the whole mixture became homogeneous.

Moreover, two samples were obtained by the addition of acrylic acid or methacrylic acid to the sample containing PVC, DBP, chlorinated paraffin, and dibutyltindilaurate to study their effect on the fire-resistance and electrical properties of this sample.

The obtained samples are denoted by G_0, G_1, G_2, . . . G_{10}. These qualitative and quantitative formulations are shown in Table II. These samples (G_0–G_{10}) were screened as fire-resistant.[9,10] The results are given in Table III.

Dielectric Measurements

Permittivity ε' and dielectric loss ε'' for the denoted samples were measured at different frequencies ranging from 100 Hz to 100 kHz. An LCR meter type AG-4311B Ando electric LTD with the test cell NFM/5T was used. The capacitance C and the loss tangent (tan δ) were obtained directly from the bridge, from which ε' and ε'' were calculated. The samples were discs of 58 mm diameter and of 2 mm thickness. Calibration of the apparatus was carried out using standard samples (Trolitul, glass, and air) of thickness 3 mm; the accuracy for ε' was ±1%, and for ε'', ±2%. The measurements were carried out at temperatures of 20, 30, and 40°C using an ultrathermostat.

Conductivity Measurements

The electrical conductivity (σ) of the investigated samples was measured by the application of Ohm's law using the test cell NFM/5T. A power supply unit GM 45161/01 from Philips (The Netherlands) was used. The potential difference V between the plates holding the sample and the current I flowing through it was measured by a multimeter-type URI 1050 from Rohode and Schwarz, Germany. The electrical conductivity was calculated using the equation

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

where d is the thickness of the sample (m) and A is its surface area (m^2).

RESULTS AND DISCUSSION

Poly(vinyl chloride) (PVC) may be considered itself as non-flammable, but when plasticized with a plasticizer such as dibutylphthalate (DBP), this property is depressed, due to the flammability of the plasticizer when used in high proportion. On the other hand, PVC is known to have kinetically rigid chains. On the addition of polar plasticizers such as DBP, 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. Since the appearance of dipole segments and dipole groups in polymers is associated with the mobility of the kinetic units of the macromolecular chain, therefore, the PVC–DBP system should exhibit higher mobilities.[11]

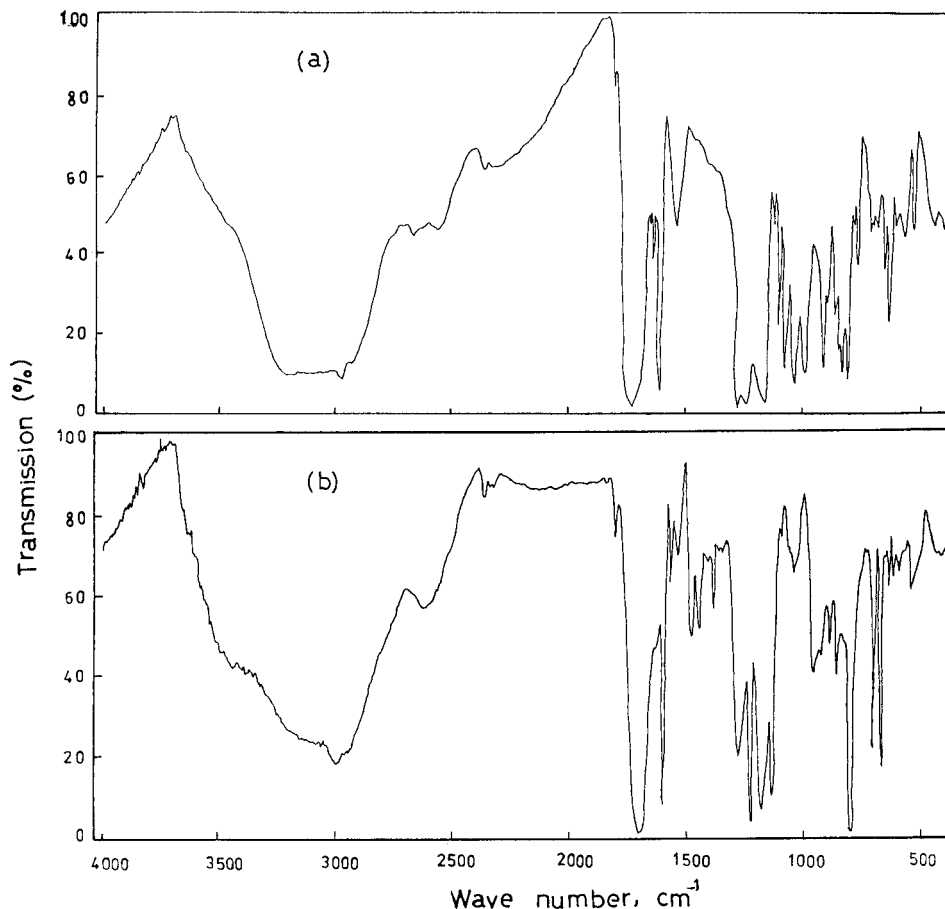In this investigation, the treatment of PVC

Figure 1   (a) IR spectrum of adduct A; (b) IR spectrum of adduct B.

with a polar plasticizer (DBP) increases its flammabiliy, but when it is modified with a wide variety of fire-retarding modifiers (adduct A or adduct B) prior to curing, this flammability is depressed. Moreover, the electrical properties of sample G_0 were studied in the presence of different concentrations of adduct A or adduct B in order to obtain a plasticized PVC of good electrical insulation character.

The presented data given in Table III show that the weight loss percent of the sample G_0 is 24.88%, the weight loss percent of the sample G_1 (containing acrylic acid) is 33.73%, and that of the sample G_2 (containing methacrylic acid) is 35.74%. This means that the fire resistance of these three samples is in the order $G_0 > G_1 > G_2$. This indicates that the presence of the carboxylic group in sample G_1 and methyl and carboxylic groups in sample G_2 increases flammability in the order $G_1 < G_2$, which is in concordance with Rosser.[12]

In the present work, a polymer (PVC), plasticizers (DBP and a chlorinated paraffin), a fire-retarding modifier (adduct A or adduct B), and a heat stabilizer (dibutyltindilaurate) were formulated together to form fire-resistant samples. The data presented in Table III show that the fire-resistance property improves gradually with increasing the amount of adduct A or adduct B from 0.5 to 2.0 g. This may be attributed to the fact that the halogenated compounds depend on the production of HCl which is a noncombustible gas as well as a flame-propagation inhibitor. HCl is known to inhibit flame propagation by a free-radical mechanism.[6,12] It is also clear from Table III that samples G_3, G_4, G_5, and G_6 (containing adduct A, having a carboxylic group and 60.8% chlorine from its structure) have a fire resistance better than that of samples G_7, G_8, G_9, and G_{10} (containing adduct B, having methyl and carboxylic groups and 58.4% chlorine from its structure). This indi-
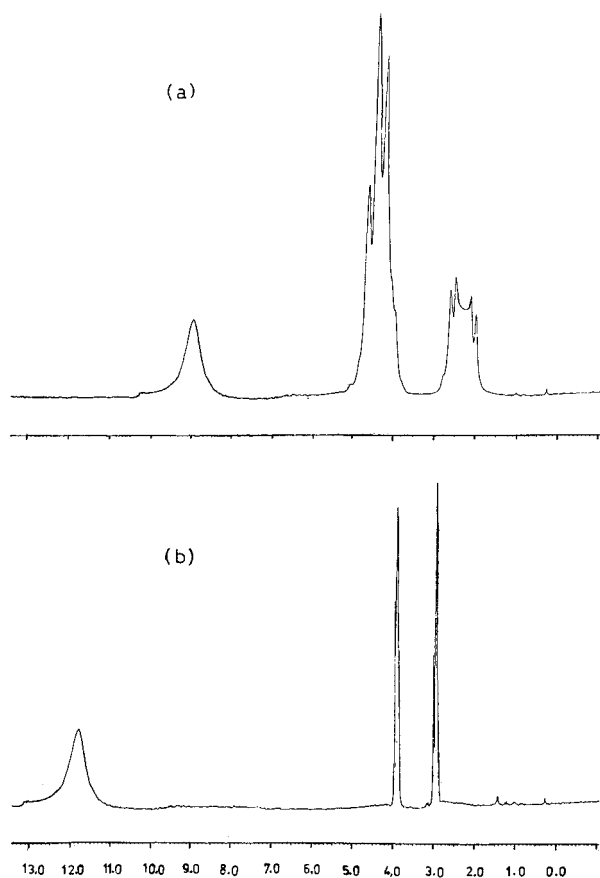
Figure 2 (a) NMR spectrum of adduct A; (b) NMR spectrum of adduct B.

cates that the presence of a methyl radical in samples G_7, G_8, G_9, and G_{10} (containing adduct B) increases flammability, i.e., flammability decreases by the lowering or absence of the methyl radical.[12] At the same time, the chlorine content may be responsible for the high flame retardation of samples G_3, G_4, G_5, and G_6 when compared with other samples, due to the fact that the presence of halogen compounds can reduce flammability.[2]

The permittivity (ε') and dielectric loss (ε'') for the prepared samples (G_0, G_1, G_2, . . . G_{10}) over the frequency range from 100 Hz to 100 kHz at different temperatures from 20 to 40°C were studied. The results obtained for ε' and ε'' vs. the frequency for these samples at the different temperatures are shown in Figures 3 and 4.

It is evident from Figures 3 and 4 that ε' increases with increasing temperature and decreases with increasing frequency. Similar behavior was noticed before in the literature.[13] The in-

crease of ε' with temperature can be explained by the increase in the mobility of polar groups, the 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 (3) shows that the value of ε' increases by the addition of acrylic acid to sample G_0 which may be due to the presence of the polar carboxylic group. Also, ε' is slightly affected by an increase in adduct A content to 1.0 g and then increases with a further increase up to 2.0 g. However, Figure 4 reveals that the value of ε' decreases by the addition of methacrylic acid to sample G_0. This may be because the CH_3 group in methacrylic acid exerts an electron-repelling effect which decreases the magnitude of electron displacement in the O—H bond and, accordingly, renders the ionization of H more difficult. Also, ε' decreases with increasing adduct B content, especially at the very low frequency region. This could be attributed to some steric hindrance due to the presence of a methyl group in the same position of a carboxylic group in adduct B despite the presence of a number of polar groups or atoms that are capable of orientation in an electric field. This restricts the rotation of the molcules to some extent. The value of ε' reaches 7.0 at 1 kHz and 20°C for sample G_{10}. This result is in agreement with the data of standard plasticized PVC insulated wire[14] ($\varepsilon' = 5-7$ at 1 kHz and 25°C) and supported by the results of PVC–DOP systems[13] ($\varepsilon' = 4.5-6.5$ at 1 kHz and 20°C).

It is apparent from Figures 3 and 4 that ε'' is greatly increased at higher temperatures, especially in the lower-frequency region. Moreover, Figure 3 reveals that the value of ε'' in the lower-frequency region is much increased by the addition of acrylic acid to sample G_0 and also increases with increasing adduct A content. However, Figure 4 shows that the value of ε'' in the lower-frequency region decreases by the addition of methacrylic acid to sample G_0 or increasing adduct B content and is slightly changed at frequencies above 10 kHz where it becomes approxi-

Table I   Properties of the Prepared Adducts

Component	Average MW	Melting Range (°C)
Adduct A	345	96–98
Adduct B	359	104–106

Table II   Formulations of Fire-Resistant Samples

Components (g)	Sample Notation										
	G_0	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9	G_{10}
Poly(vinyl chloride) (PVC)	5	5	5	5	5	5	5	5	5	5	5
Dibutylphthalate (DBP)	2	2	2	2	2	2	2	2	2	2	2
Chlorinated paraffin[a]	1	1	1	1	1	1	1	1	1	1	1
Dibutyltindilaurate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Acrylic acid	—	2	—	—	—	—	—	—	—	—	—
Methacrylic acid	—	—	2	—	—	—	—	—	—	—	—
Adduct A	—	—	—	0.5	1.0	1.5	2	—	—	—	—
Adduct B	—	—	—	—	—	—	—	0.5	1.0	1.5	2

[a] Chlorinated paraffin is considered as a secondary plasticizer.

mately the same for all samples. It reaches 0.4 at 100 kHz at the different temperatures. The decrease in the ε'' value may be due to the presence of a methyl group attached with a carboxylic group in adduct B, which partially reduces the molecular mobility.

The low-frequency losses may be due to either dc conductivity[15,16] resulting from the increase of ion mobility or the Maxwell–Wagner effect[17] as a result of an ac current 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 direct current 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 equation[18]

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

and subtracted from the values of ε'' in the low-frequency region. The data of ε'' after subtracting ε'' are plotted versus log f and represented by dashed lines as shown in Figures 3 and 4. From Figure 3 it is clear that at the different temperatures there is an absorption region extending below 100 Hz for samples G_1, G_3, G_4, G_5, and G_6. Unfortunately, we cannot give further interpretation of this region since we have no measurement below 100 Hz. Also, from Figure 4, it is clear that at the different temperatures there is an absorption region with a maximum at about 100 Hz for samples G_2, G_7, G_8, G_9, and G_{10}. It may be concluded that the low-frequency losses are not totally dc losses and that they may comprise Maxwell–Wagner losses, as the differences between the permittivies of the different ingredients in the investigated samples are relatively large.

On the other hand, the changes of the electrical conductivity (σ) of samples G_0, G_1, G_2, G_3 . . . G_{10} with temperature is shown in Figure 5. It is evident that, at lower temperatures, σ of these samples is low and increases as the temperature is increased. This increase is more pronounced in the case of samples G_1, G_3, G_4, G_5, and G_6 and may be due to the increase of the mobility of the ionic bodies that takes place as a result of the excitation by heat, leading to an increase in the conductivity of the investigated samples. At the

Table III   Fire-Resistance Test on the Prepared Samples

	Sample Notation										
	G_0	G_1	G_2	G_3	G_4	G_5	G_6	G_7	G_8	G_9	G_{10}
Weight loss (%)	24.88	33.73	35.74	23.0	17.86	11.16	7.31	23.33	19.50	14.92	15.06
Flammability	B	B	B	B	B	NB	NB	B	NB	NB	NB

B, burning; NB, nonburning.
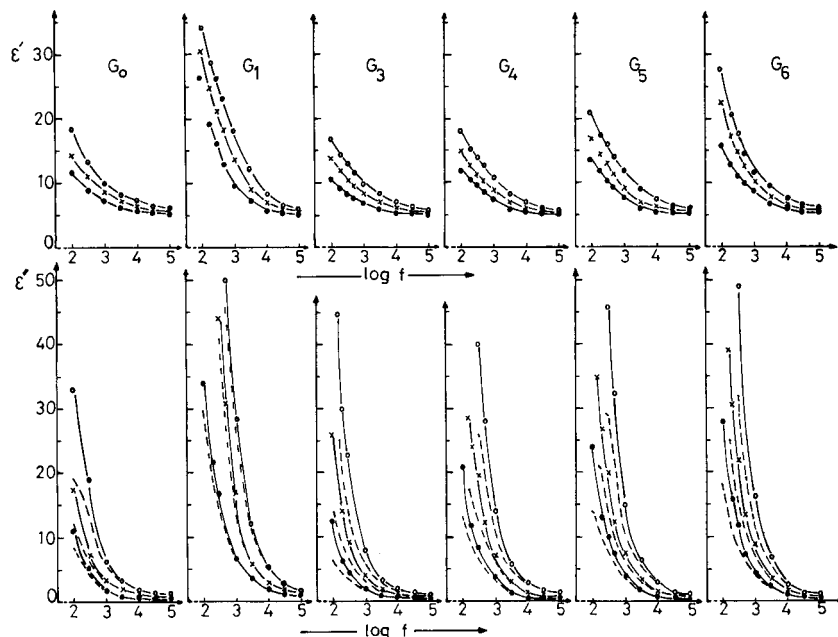
Figure 3 The permittivity (ε') and dielectric loss (ε'') versus frequency at different temperatures: ($\bullet$) 20; ($\times$) 30; ($\bigcirc$) 40°C, for the PVC–DBP–chlorinated paraffin system mixed with acrylic acid or variable proportions of adduct A (G_0, G_1, G_3, G_4, G_5, and G_6; see Table II). The dashed line represents the measured $\varepsilon'' - \varepsilon''_{dc}$.

higher temperatures, it is also probable that the chlorine ions are free to follow the external field. With respect to samples G_0 mixed with acrylic acid or adduct A (samples G_1, G_3, G_4, G_5, and G_6), Figure 5 also shows that the value of σ in-creases using acrylic acid and increases to a great extent with increasing adduct A content, espe-cially at higher temperatures. This may be attrib-uted to the increase in the orientation of the mo-bile groups or atoms. On the other hand, the value
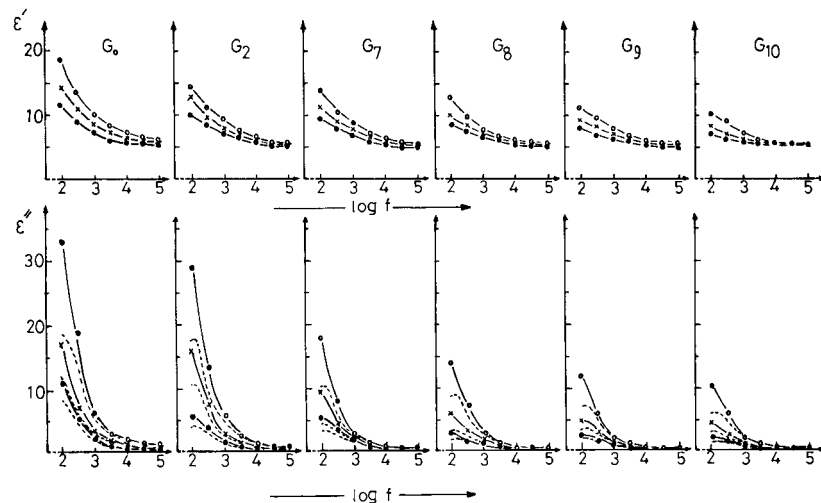

Figure 4 The permittivity (ε') and dielectric loss (ε'') versus frequency at different temperatures: ($\bullet$) 20; ($\times$) 30; ($\bigcirc$) 40°C, for the PVC–DBP–chlorinated paraffin system mixed with methacrylic acid or variable proportions of adduct B (G_0, G_2, G_7, G_8, G_9, and G_{10}; see Table II). The dashed line represents the measured $\varepsilon'' - \varepsilon''_{dc}$.
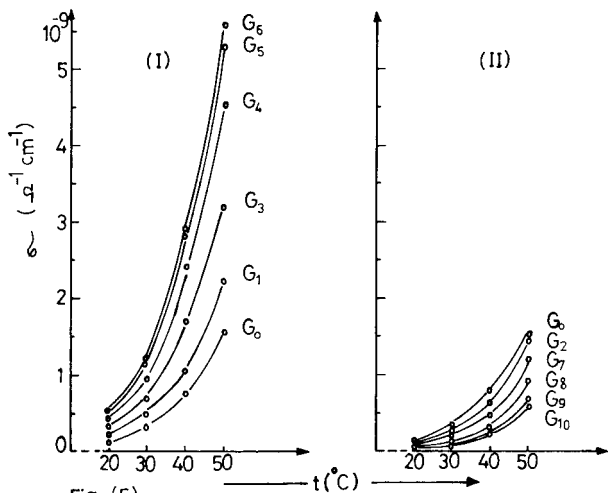
Figure 5 The relation between conductivity (σ) and temperature (t) for samples G_0, G_1, G_3, G_4, G_5, G_6 (I) and samples G_0, G_2, G_7, G_8, G_9, and G_{10} (II).

of σ for sample G_0 mixed with methacrylic acid or adduct B (samples G_2, G_7, G_8, G_9, and G_{10}) slightly decreases using methacrylic acid or increasing quantities of adduct B. This may be attributed to the presence of a methyl group in the same position with the carboxylic group in adduct B which causes some steric hindrance that par-

tially contributed to decreasing the mobility of the electric charges and, accordingly, the conductivity of these samples slightly decreases. Figure 6 shows the relation between conductivity (σ) and the content of adduct A (I′) or B (II″).

CONCLUSIONS

1. The prepared samples can be arranged according to the best fire resistance (lowest weight loss; percent nonburning) as follows:

$$G_6 > G_5 > G_{10} \simeq G_9 > G_4 > G_8 > G_3$$
$$> G_7 > G_0 > G_1 > G_2.$$

2. The rate of weight loss (%) indicates the flammability or rapidity of burning.
3. The prepared fire-resistance samples improves gradually with increasing the amount of fire-retarding modifier; [1,2,3,4, 7,7-hexachloro-5-carboxy,bicyclo(2,2,1)heptene-2] (adduct A) or [1,2,3,4,7,7-hexachloro-5-carboxy,5-methylbicyclo(2,2,1) heptene-2] (adduct B).
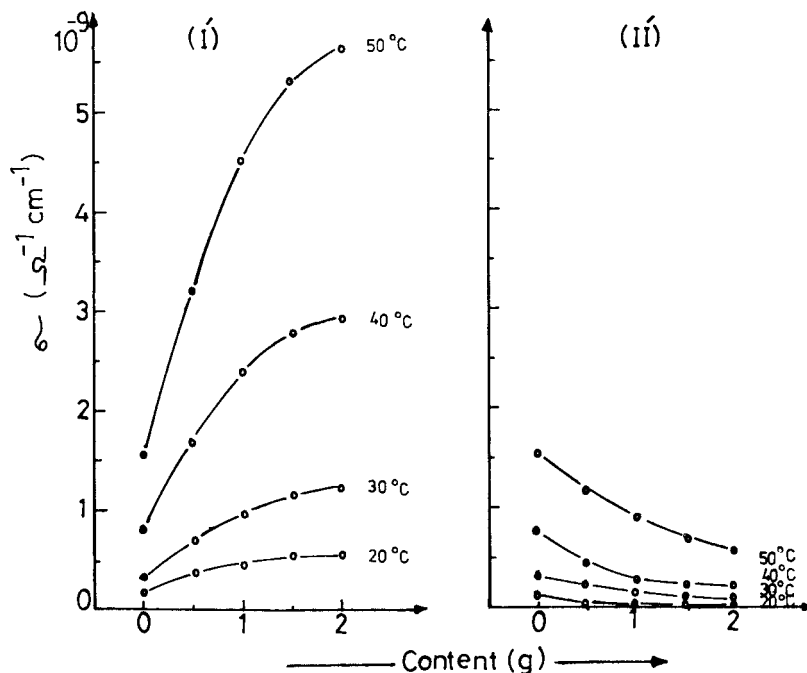4. The presence of chlorine atoms in a fire-

Figure 6 The relation between conductivity (σ) and the content of adduct A (I′) or B (II′).

retarding samples decreases flammability, while the presence of methyl and carboxylic groups increases it.

5. The electrical properties (permittivity, dielectric loss, and electrical conductivity) of a plasticized PVC (sample G_0) could be improved by the addition of adduct A and to a greater extent by adding adduct B, especially at frequencies higher than 10^4 Hz, making it of interest as a practical wire insulator.

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