

Electrical Properties of Chlorinated Atactic Polypropylene (CAPP) and PVC–DOP–CAPP System

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Synopsis

The electrical properties, such as dielectric properties and volume resistivity, of chlorinated atactic polypropylene (CAPP), obtained by thermal chlorination of APP, have been studied. The results show that dielectric constant, loss tangent, and volume resistivity of the chlorinated samples increase with the increase in degree of chlorination. The effect of CAPP as secondary plasticizer in the PVC–DOP system has also been studied. Dielectric study of PVC compounds shows a single relaxation peak, indicating no phase separation. In the case of PVC compounds, it has been observed that with the increase in CAPP content in PVC compounds dielectric constant and loss tangent decrease whereas volume resistivity increases. The increase in volume resistivity was further supported by the increase in activation energy value, obtained from volume resistivity vs. $1/T$ plot.

INTRODUCTION

Chlorinated paraffins are generally used as a secondary plasticizer for poly(vinyl chloride) (PVC) in conjunction with a phthalate group plasticizer such as dioctyl phthalate (DOP).¹ Due to their low volatility, these materials are specially used in cable compounds where high temperature performance is required. Chlorinated atactic polypropylene (CAPP) has been attempted as secondary plasticizer for PVC.² Although many attempts have been made to evaluate the electrical properties of PVC and chlorinated polyethylene (CPE), no work has been reported regarding the electrical properties of CAPP and its blend with PVC–DOP system.

The present study was undertaken to evaluate the electrical properties of CAPP having various degrees of chlorination and its effect as secondary plasticizer in the PVC–DOP system.

EXPERIMENTAL

Samples of CAPP having various degrees of chlorination and synthesized at different conditions by thermal chlorination were used.³

Suspension grade PVC resin of K-67 value supplied by National Organic Chemical Industries Limited, Bombay, India, was directly used without any further purification. Tribasic lead sulfate (TBLS) and calcium stearate as heat stabilizer and lubricant respectively for PVC were supplied by Ajanta Electric Co., New Delhi, India. DOP (Fluka) was used as plasticizer for PVC.

TABLE I
Formulation Containing Different Parts of DOP and CAPP (53.5% Cl)

Ingredients	Parts by weight					
	PVC I	PVC II	PVC III	PVC IV	PVC V	PVC VI
PVC	100	100	100	100	100	100
DOP	30	60	30	30	30	30
CAPP	—	—	5	10	20	30
TBLS	5	5	5	5	5	5
Ca. stearate	1	1	1	1	1	1

Sample Preparation

For measuring the electrical properties in the case of CAPP, samples were prepared in the form of pellets. The thickness ranged from 0.2 to 0.3 mm. In the case of PVC-DOP-CAPP system, the compositions containing different parts of CAPP and other additives were premixed after drying in a vacuum oven for 6 h at 60°C to expel any moisture present (Table I). The premixed compositions were extruded in a twin screw extruder, Brabender Plasticorder PLE-651, with L/D of 5 at a screw speed of 25 rpm and keeping the temperature profile as 170°C (feed zone), 175°C (mixing zone), and 180°C (die zone). The thick continuous strands were chopped and specimens for various tests were prepared by compression moulding on Carver Laboratory press, at 185°C and 50 kg/cm² pressure. The thickness of different samples ranged from 0.1 to 0.15 mm.

Aluminium electrodes of circular shape with area of 0.636 cm² were vacuum deposited on both sides of these sheets and pellets for dielectric and volume resistivity measurements.

Dielectric ac Bridge Measurement

The capacitance and loss angle ($\tan \delta$) of the samples were measured with HP 4192 LF Impedance analyzer in the frequency range of 10³–10⁶ Hz at different fixed temperatures. Dielectric constant was calculated from the measured value of capacitance C by using the relationship

$$\text{Dielectric constant } \epsilon' = \frac{C \cdot d}{\epsilon_0 \cdot A}$$

where C = measured value of capacitance, ϵ_0 = permittivity of free space, d = thickness of the sample, and A = area of the sample.

Electrical Volume Resistivity Measurements

The steady-state current as a function of voltage at different fixed temperature was measured by using Keithley 610C electrometer. The measurement cell was the same which was used for dielectric measurement. The volume resistivity (V_R) was calculated by using the relation

$$V_R = \frac{A \cdot V}{d \cdot I}$$

where A = area of the sample, V = voltage applied across the material, d = thickness of the material, and I = measured current.

RESULTS AND DISCUSSION

Dielectric Studies

Dielectric Properties of CAPP

In Table II are presented the values of dielectric constant (ϵ'), loss tangent ($\tan \delta$), and onset temperature (T_{onset}) for the initial rise of loss tangent values of CAPP having different chlorine content. It can be seen from the results that ϵ' , $\tan \delta$, and T_{onset} increase with increase in degree of chlorination.

APP is a nonpolar, tacky, waxy hydrocarbon polymer having low T_g (-13°C).⁴ With the introduction of polar chlorine atoms in the structure, ϵ' , and $\tan \delta$ increase. The dipole-dipole interaction and H bonding increase in CAPP with increased chlorination, which in turn results in the reduction in free volume and consequently leads to an increase in glass transition temperature (T_g).⁵ Since dielectric constant and $\tan \delta$ are dependent on polarity of a molecule, the magnitude of these factors increases with the increase in degree of chlorination. Moreover, an increase in H bonding due to increased degree of chlorination will result in more chain interactions. As a consequence, an increase in proton transfer along the H-bond chain will occur resulting in an increase in loss tangent.⁶ Also, T_{onset} , which indicates the occurrence of segmental mobility, increases with increasing chlorine content. The parameter T_{onset} is used here in place of loss peak temperature, T_{max} , simply because of uncertainty in locating peak temperature for the observed broad loss peak. The occurrence of broad loss peaks might be due to nonuniform structure of the polymer. This nonuniformity of structure arises due to random chlorination.

Dielectric Properties of PVC-DOP-CAPP Systems

PVC containing varying amounts of CAPP and DOP has been subjected to dielectric studies. The variation of $\tan \delta$ and dielectric constant as a function of temperature with frequency have been studied and the results have been presented in Figure 1 only for sample, PVC IV. In the case of other samples, a

TABLE II
Results of the Dielectric Studies of Chlorinated APP Samples

Chlorine content (%)	ϵ' at 10^4 Hz at 30°C	$\tan \delta$ at 10^4 Hz at 30°C	T_{onset} for $\tan \delta_{\text{max}}$ ($^\circ\text{C}$)
35.0	3.11	0.0032	60
42.5	3.65	0.0052	70
53.5	4.42	0.0073	80

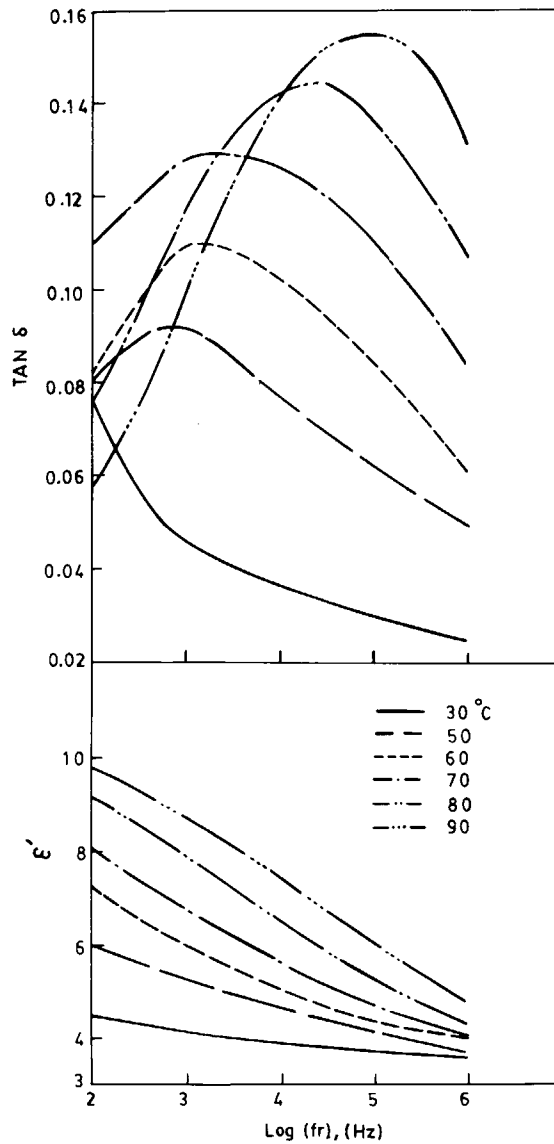


Fig. 1. Variation of ϵ' and $\tan \delta$ with frequency at various temperatures for PVC IV.

similar type of spectrum has been obtained. It can be seen from Figure 1 that ϵ' gradually increases with increasing temperature. This phenomenon can be explained on the basis of increase in molecular mobility with increase in temperature. At temperatures below the glass transition temperature, there will be fewer number of dipoles that can orient with the field. As the temperature increases, the molecular mobility increases and more dipoles can orient themselves in the field direction; hence the dielectric constant increases with the increase in temperature.

The $\tan \delta$ vs. log frequency plots (Fig. 1) for all the systems give only one peak implying that a single relaxation phenomenon is operative and no phase separation occurs.⁷

TABLE III
Results of Dielectric Studies of PVC-DOP-CAPP Samples

Sample name	Plasticizer content (phr ^a)		ϵ' at 10 ³ Hz, 30°C	tan δ at 10 ³ Hz, 30°C	T_{\max} at 10 ³ Hz, 30°C
	DOP	CAPP			
PVC I	30	—	4.46	0.0690	60
PVC II	60	—	6.23	0.1184	—
PVC III	30	5	4.34	0.0578	70
PVC IV	30	10	4.23	0.0560	70
PVC V	30	20	4.18	0.0416	70
PVC VI	30	30	4.00	0.0416	70

^aParts per 100 parts of PVC.

The tan δ vs. frequency plots (Fig. 1) at various temperatures show that the tan δ shifts towards higher frequency with increasing temperature. This type of observation is very common in dielectric studies. Thus, according to Gupta,⁸ increase in temperature facilitates the mobility of chain and thereby reduces the relaxation time (or increases the relaxation frequency). The peaks are broad indicating the heterogeneous nature of CAPP and PVC. Similar types of curves for PVC have been cited in literature and the reason for this has been attributed to structure heterogeneity.⁹

The variation of dielectric constant, tan δ , and relaxation temperature with varying CAPP content at 10³ Hz are presented in Table III. These results show that (i) the magnitude of dielectric constant and tan δ decreases with increasing CAPP content, and (ii) the relaxation temperature initially increases and then remains constant as the CAPP content increases. PVC is a polar polymer having dielectric constant equal to 4.55 at 10³ Hz.¹⁰ PVC compound containing 30 parts DOP has ϵ' equal to 4.46, whereas 60 parts DOP has ϵ' equal to 6.23. However, on addition of CAPP having dielectric constant equal to 4.42 at 10⁴ Hz, the effective dielectric constant PVC compound decreases with increase in CAPP content. The decrease in tan δ is an indication of plasticization effect.¹¹ From the literature^{8,9} one can see that the T_{\max} and T_g values are directly related. Incorporation of a primary plasticizer such as DOP leads to a decrease in T_{\max} value and, therefore, in T_g values of PVC compounds. The effectiveness of secondary plasticizer as compared to a primary plasticizer is always less.¹² Due to these reasons, incorporation of CAPP, as secondary plasticizer for PVC, shows in the present study that T_{\max} values of such PVC compounds as compared to that obtained with DOP as plasticizer are higher. However, with increase in CAPP content from 5 to 30 parts there is no change in T_{\max} values in the PVC compound. It may be borne in mind that the decrease in effective DOP content by incorporation of 30 parts CAPP is only to the tune of 7% compared to samples containing only 30 parts DOP.

The higher values of T_{\max} of all the systems are due to the effect of frequency of measurement.⁸ Similar types of results have been observed by others¹³ in the case of PVC compound containing other plasticizers.

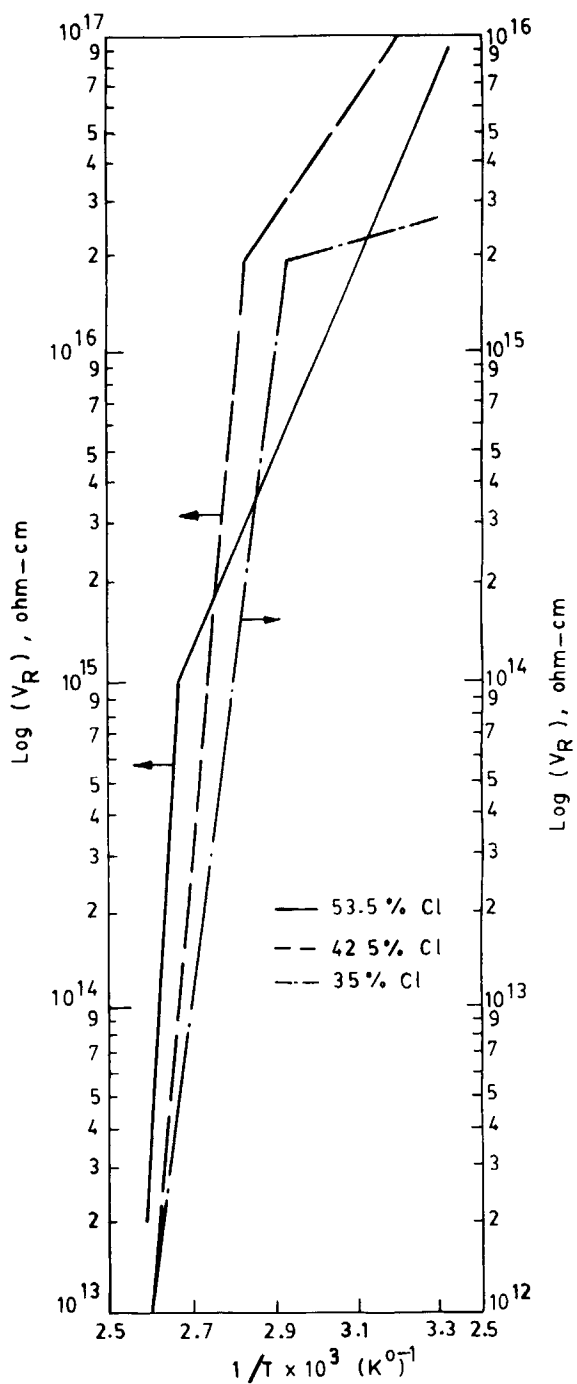


Fig. 2. Variation of volume resistivity with temperature for CAPP having different chlorine content.

TABLE IV
Results of the Resistivity Studies of Chlorinated APP Samples

Chlorine content (%)	V_R (Ω cm) at 10 kV/cm, 30°C	$T_{\text{deflection}}$ (°C)	E_a (kcal/mol)
35.0	2.65×10^{15}	68	37.5
42.5	3.18×10^{15}	80	64.9
53.5	6.70×10^{15}	101	85.4

Electrical Resistivity Studies

Volume Resistivity of CAPP

The variation of steady state volume resistivity (V_R) with temperature, measured at a constant field of 10 kV/cm, for CAPP having various degrees of chlorination are shown in Figure 2, which shows that for all the three samples, with the increase in temperature, the V_R initially decreases slowly, and then a point of deflection occurs after which the decrease in V_R becomes more rapid.

V_R , the reciprocal of volume conductivity, depends on the presence of free charges (electrons or ions) and their mobility. With rising temperature the resistivity decreases owing to increasing mobility of the free charges.¹⁴ Many workers have reported that the point of deflection in resistivity versus temperature plot is an indication of T_g .¹⁵ This is obviously due to the fact that at a temperature above the glass transition temperature ionic mobility increases owing to the considerable mobility of the chain segments; as a result, the resistivity decreases. The temperatures corresponding to the point of deflection in resistivity vs. temperature plot (Fig. 2) are presented in Table IV. These results show that deflection temperature values and, therefore, T_g values increase with the increase in degree of chlorination.

The values of activation energy calculated from the slope (at temperature above the deflection point) of $\log V_R$ vs. $1/T$ plot are given in Table IV along with the values of V_R for CAPP samples having various degrees of chlorination. These results suggest that with the increase in the degree of chlorination, the intermolecular interaction increases owing to the formation of secondary forces of greater magnitude resulting in decrease in the chain mobility. Similar trend has been reported by others¹⁶ for chlorinated PE.

Volume Resistivity of PVC-DOP-CAPP System

In Figure 3 is presented the variation of volume electrical resistivity V_R with temperature measured at a constant field of 10 kV/cm, for the PVC-DOP-CAPP system having various parts of CAPP (53.5% Cl). In Table V are presented the values of activation energy responsible for resistance, calculated from the slope of $\log V_R$ vs. $1/T$, and the variation of V_R with respect to CAPP content in the PVC-DOP system. From Figure 3, it can be seen that, in all the cases, V_R decreases with increasing temperature of measurement. This is attributable to the mobility of molecular chains as mentioned earlier.

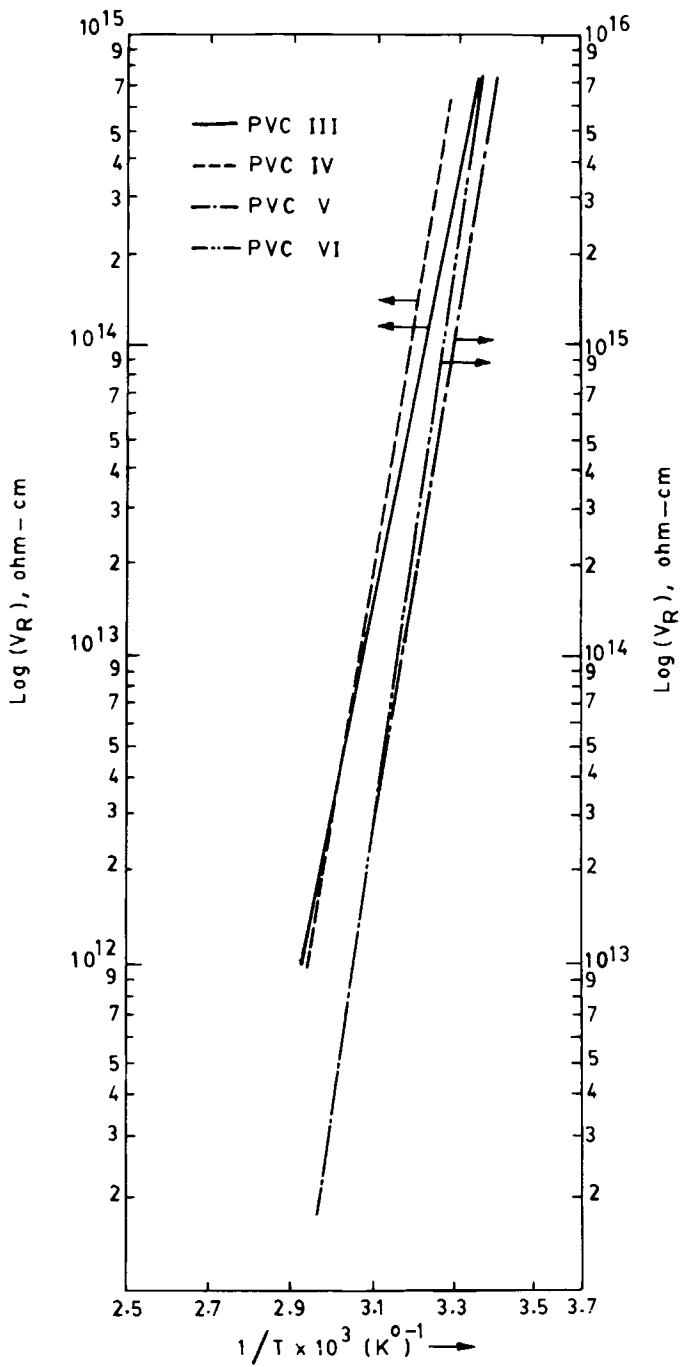


Fig. 3. Variation of volume resistivity with temperature for various PVC compounds.

TABLE V
Results of the Electrical Volume Resistivity Studies of PVC-DOP-CAPP Samples

Sample name	Plasticizer content (phr)		V_R (Ω cm) at kV/cm, 30°C	E_a (kcal/mol)
	DOP	CAPP		
PVC I	30	—	7.50×10^{14}	—
PVC II	60	—	3.53×10^{11}	—
PVC III	30	5	4.30×10^{14}	30.9
PVC IV	30	10	4.24×10^{14}	39.9
PVC V	30	20	1.72×10^{15}	40.4
PVC VI	30	30	2.54×10^{15}	44.8

Results in Table V shows that, with increase in CAPP content, both activation energy and volume resistivity increase. Pure PVC is a material of high volume resistivity of the order of 10^{16} Ω cm.¹⁷ On the addition of plasticizer (DOP), V_R decreases due to the enhanced molecular mobility of the polymeric chain.¹⁵ Thus, PVC compound containing 30 parts DOP has V_R equal to 7.5×10^{14} Ω cm whereas 60 parts DOP has V_R equal to 3.53×10^{11} Ω cm. Addition of CAPP, as secondary plasticizer, to PVC-DOP system should further decrease V_R value. But the results in Table V show that V_R increases with increase in CAPP content. CAPP used in the present system has high chlorine content (53.5% Cl) and high resistivity value (Table IV). Addition of this material obviously will augment the V_R and activation energy values.

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Received May 1, 1989

Accepted May 8, 1989