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THERMAL STUDIES ON CHLORINATED ATACTIC POLYPROPYLENE

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ABSTRACT

Thermal behavior of chlorinated atactic polypropylene (CAPP) obtained by thermal chlorination of atactic polypropylene was evaluated by thermogravimetric analysis and differential thermal analysis (DTA). It was found that the initial decomposition temperature, integral procedural decomposition temperature, activation energy, and char yield increase with an increase in chlorine content. The thermal stability of CAPP was found to be lower in air than in nitrogen. This has been ascribed to thermooxidative degradation in air. DTA study shows that onset decomposition temperature, glass transition temperature, and polymer melting temperature increase with increasing degree of chlorination. The possible reasons for the phenomena are discussed.

INTRODUCTION

Atactic polypropylene (APP) has been subjected to chlorination by several workers [1-7] to enhance its application properties. One of the possible areas in which chlorinated atactic polypropylene (CAPP) can be used is in compounding of poly(vinyl chloride) (PVC). There is a potential for CAPP acting as a secondary plasticizer for PVC. PVC compounds are usually processed at an elevated temperature, and so the thermal stability of such a plasticizer is necessary. Though several well-known studies have been done on the thermal degradation of PVC [8, 9], no study has so far been made on the thermal stability of CAPP.

The present study was undertaken to evaluate the thermal characteristics of CAPP.

EXPERIMENTAL

Samples of CAPP of varying degrees of chlorination synthesized at different conditions by thermal chlorination were used.

Thermogravimetric Analysis (TGA)

TGA studies were carried out on a Du Pont 1090 thermal analyzer with a 951-TG module, both under nitrogen and in static air. A heating rate of 10°C/min, a sample size of 10 ± 1 mg, and a nitrogen flow of 60 cm^3/min were maintained.

From the thermograms obtained, initial decomposition temperature (IDT) and integral procedural decomposition temperature (IPDT) were calculated according to the method described by Doyle [10].

Activation energies for the degradation, both under nitrogen and in static air were obtained by using the modified Freeman and Caroll method [11].

Differential Thermal Analysis (DTA)

DTA was carried out by using a Stanton Redcroft differential thermal analyser. 9 ± 1 mg of sample was heated in air at a heating rate of 10°C/min from ambient temperature to 450°C. Onset decomposition temperature (ODT). glass-transition temperature (T_g), and polymer melting temperature (PMT) were obtained from the DTA curves.

CAPP samples were prepared by the thermal chlorination technique. Chlorination parameters such as time, temperature, chlorine flow rate, and APP concentration were suitably varied to obtain a degree of chlorination varying from 25 to 53.5 wt%. APP is a tacky material, and on increasing the degree of chlorination, the tackiness decreases and yields a material which is brittle above 25 wt% Cl. CAPP samples, irrespective of degree of chlorination, have been found to be stable at ambient temperature.

RESULTS AND DISCUSSION

Thermogravimetric Studies

CAPP samples of various degrees of chlorination were thermogravimetrically analyzed in a nitrogen atmosphere as well as in static air. Both primary thermograms and derivative thermograms are presented in Figs. 1 and 2. From these results the temperatures for various levels of weight loss, IDT, and IPDT were calculated; they are presented in Table 1.

Both IDT and IPDT are higher in nitrogen than in air (see Fig. 3). In air the thermal degradation is accompanied by thermooxidative degradation, thus lowering both the IDT and the overall thermal stability, as measured by IPDT.

With increasing chlorine content in CAPP there is an increase in the thermal stability both in nitrogen and in air (Fig. 3). It is well known [12] that HCl

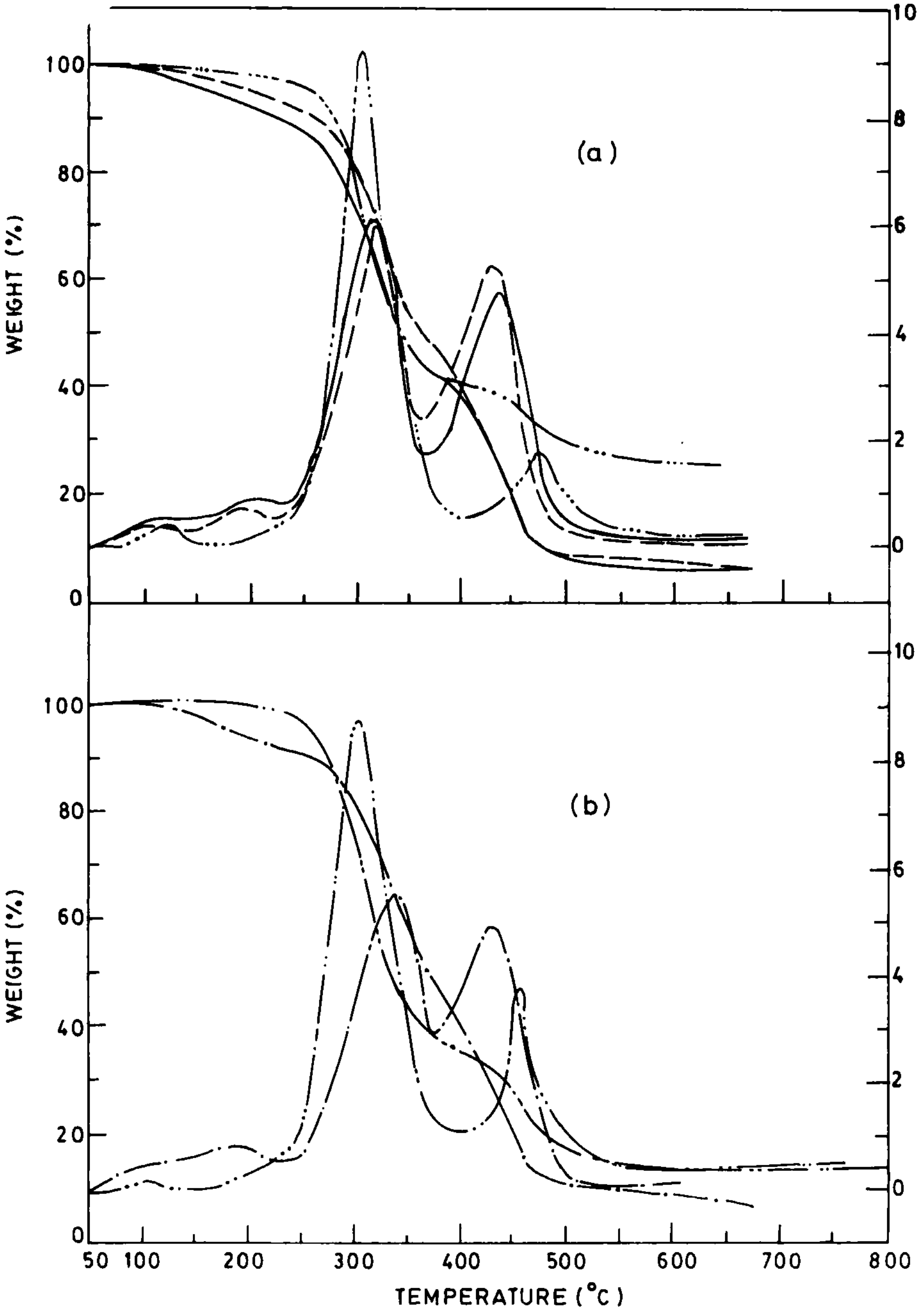


FIG. 1. TGA and DTG thermograms of CAPP in nitrogen. (a) (—) 25.1 wt% Cl, (- -) 28.0 wt% Cl, and (- ••• -) 53.5 wt% Cl. (b) (- • -) 35.0 wt% Cl and (- •• -) 42.5 wt% Cl.

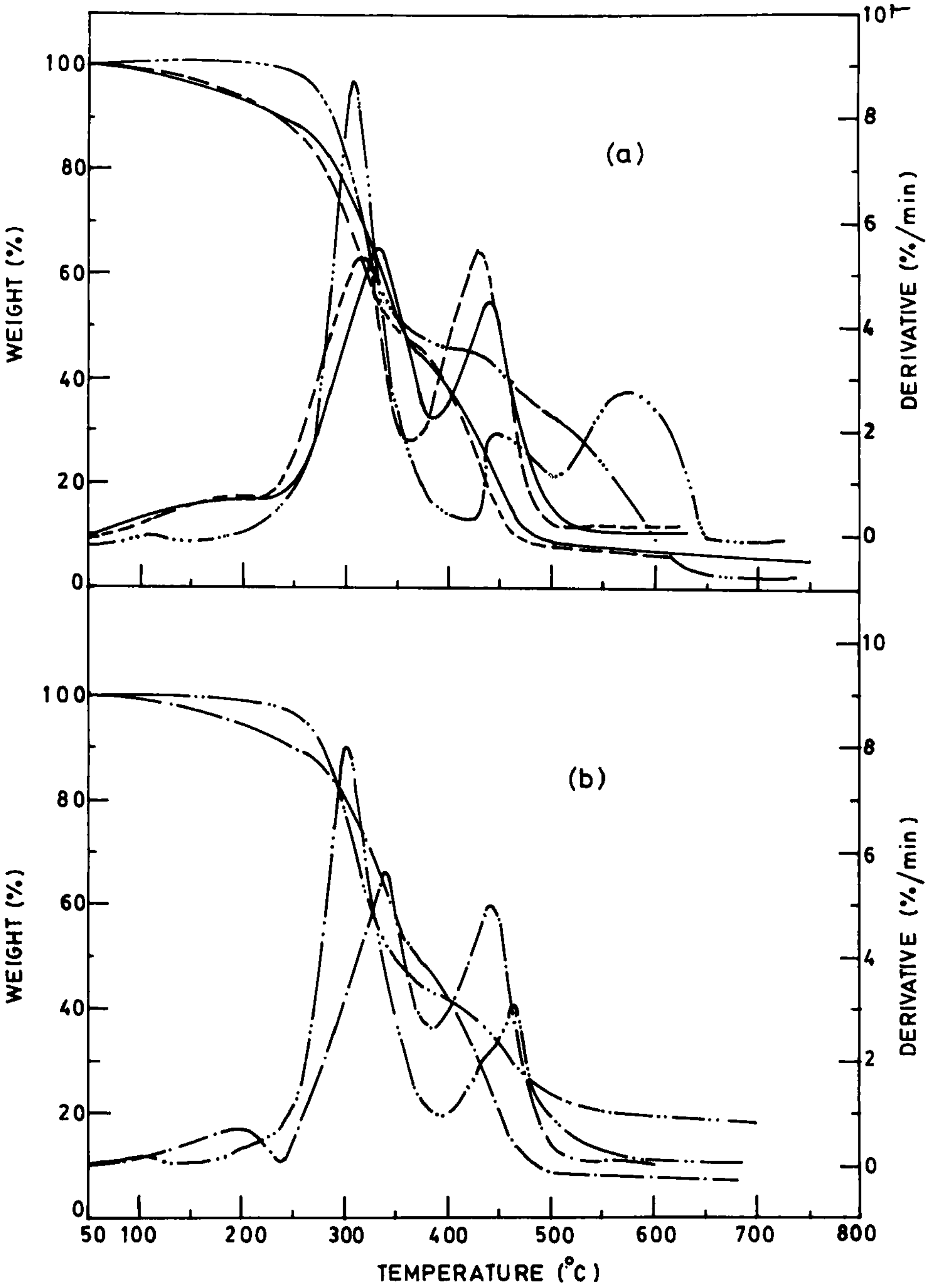


FIG. 2. TGA and DTG thermograms of CAPP in air. (a) (—) 25.1 wt% Cl, (- -) 28.0 wt% Cl, and (- ... -) 53.5 wt% Cl. (b) (- . -) 35.0 wt% Cl and (- .. -) 42.5 wt% Cl.

TABLE 1. Results of Thermogravimetric Analysis of CAPP with Different Degrees of Chlorination

		Temperature at various wt% losses, °C					
Cl, wt%	Atmosphere	10	30	50	70	IDT, °C	IPDT, °C
25.1	N_2	230	315	350	430	261.6	390
	Air	225	315	350	425	240	345.2
28.0	N_2	270	330	365	425	269.6	404.5
	Air	240	310	355	420	244	377.2
35.0	N_2	265	330	376	430	265	397.9
	Air	250	325	370	430	261.8	393.4
42.5	N_2	285	310	340	455	273.7	446.9
	Air	280	310	340	465	269.7	395.5
53.5	N_2	290	315	345	505	280	453.9
	Air	290	320	360	525	277.1	400

evolves during the degradation of halogenated organic compounds, which in turn cuts off the oxygen supply to the degrading mass, thus preventing thermooxidative degradation. In the case of chlorinated PVC (CPVC), it has also been reported that there is an increase in thermal stability with increasing chlorine content [13].

This increase in thermal stability with increasing chlorine content of CAPP is manifested in higher activation energies (E_a) (Fig. 4). These activation energies were obtained by considering the first stage of degradation. The overall thermal stability increases with increasing chlorine content, resulting in a higher order of reaction (Table 2), which indicates a slower rate of reaction.

Chlorination of APP leads to a heterogeneous product. Substitution of chlorine can take place in all the three types of H-atoms, i.e., tertiary, secondary, and primary. If only tertiary hydrogens could have been replaced by chlorine atoms, then a structure similar to that of poly(α-methyl vinyl chloride) would have been formed. However, irrespective of the degree of chlorination and the reaction conditions, it was found that all three positions are attacked due to the small differences in their reactivities [14]. This was confirmed by IR and ^{13}C-NMR studies. Several other authors reported similar results [15, 16].

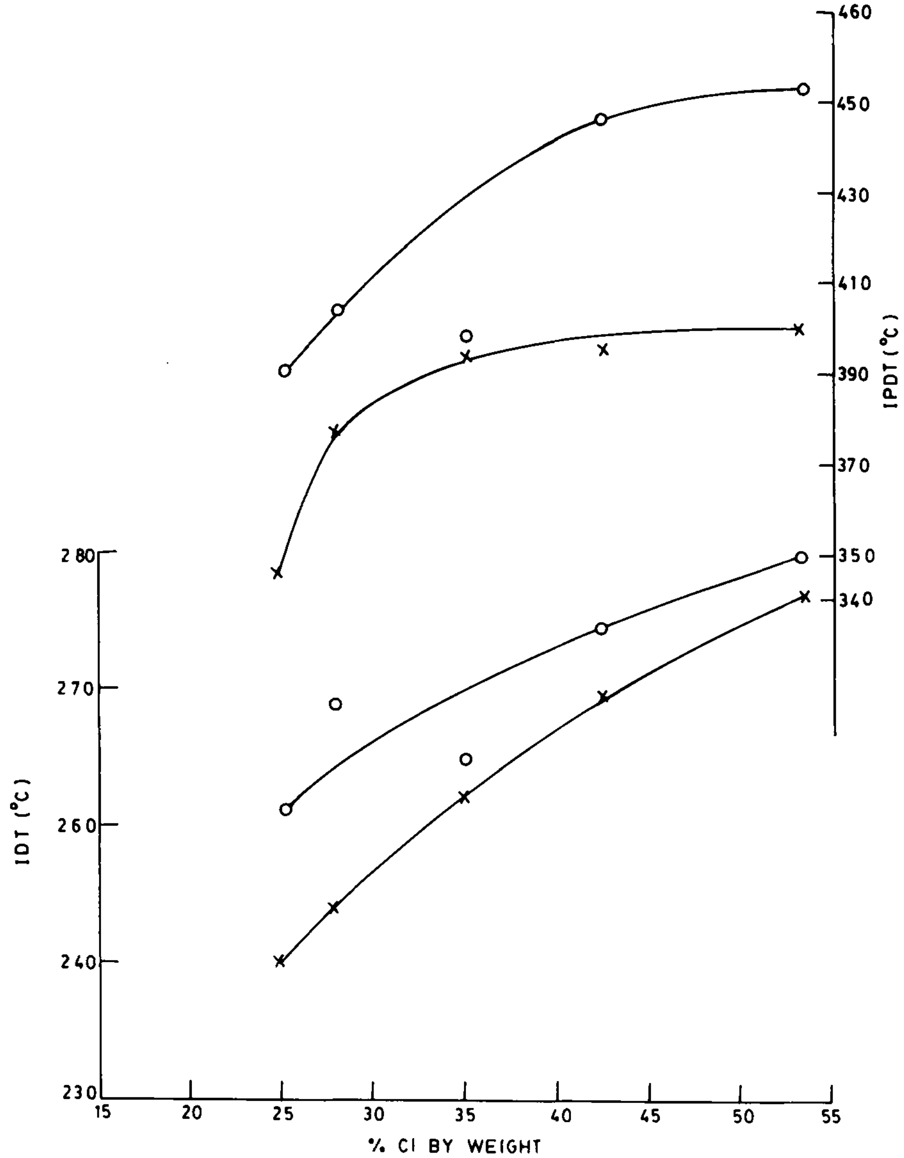


FIG. 3. Variation of IDT and IPDT with wt% Cl in CAPP: (○) in nitrogen and (X) in air.

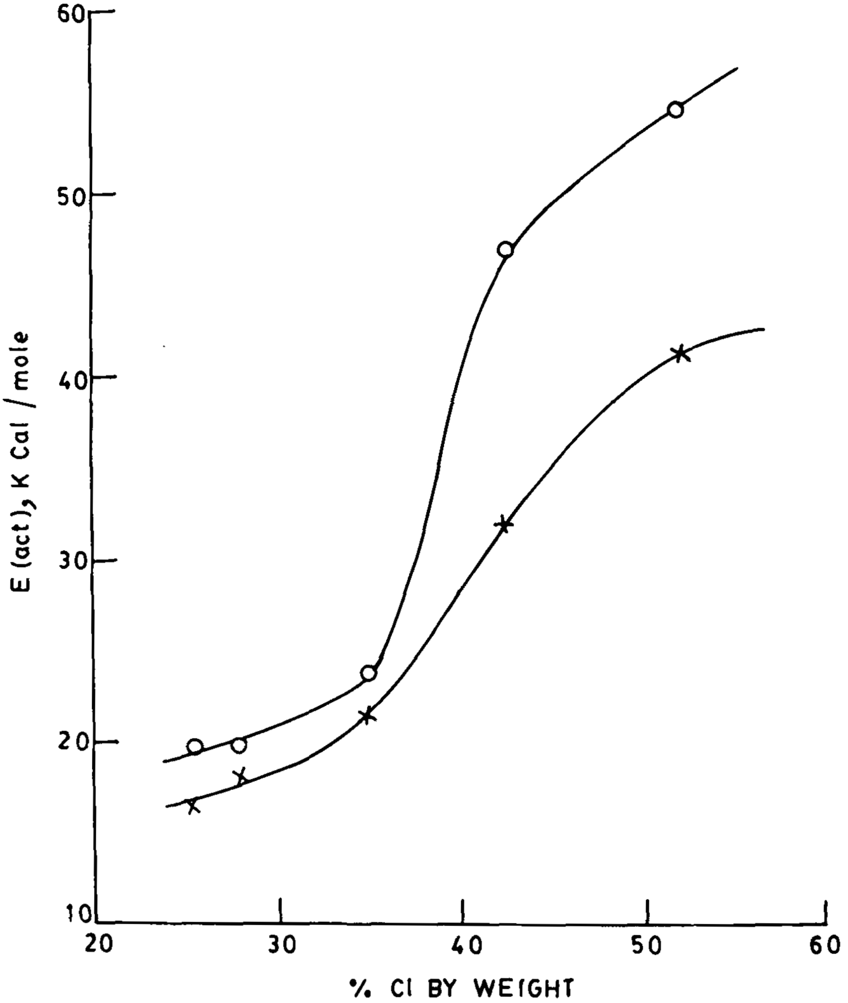


FIG. 4. Variation of E_a with wt% Cl in CAPP: (○) in nitrogen and (X) in air.

TGA study of PVC gave IDT values of 286 and 280°C in N_2 and air, respectively. Though the structure of the material of the present study is not similar to that of PVC, the IDT is similar for CAPP with a higher degree of chlorination. The IDT is governed by the ease of decomposition of the weakest bond

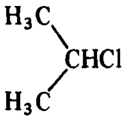
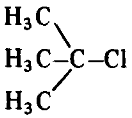
TABLE 2. Order of Reaction for CAPP from Kinetic Studies

	Order of reaction	
Cl, wt%	N_2	Air
25.1	2.3	1.09
28.0	2.92	1.52
35.0	3.16	2.25
42.5	6.3	3.4
53.4	7.3	2.77

in the material. Therefore, in the case of PVC, an elimination takes place involving either an allylic chlorine atom, a tertiary chlorine atom, or an oxygen-containing group [17]. Degradation involving an oxygen-containing group does not take place in CAPP as IR spectra show the absence of such a group. In general, PVC shows a three-step TGA thermogram [18].

Comparison of the results of the present study with those of PVC degradation indicates that CAPP thermal degradation follows a course similar to that of PVC. In the case of PVC, elimination of HCl involving the allylic chlorine atom leads to acid-catalyzed "zipper"-type reaction with the formation of conjugated double bonds. However, a "zipper"-type reaction is not possible in the case of CAPP, due to structural heterogeneity. Among the three types of bonds, i.e., $\equiv C{-}Cl$, $=CHCl$, and $-CH_2Cl$, the stability of $\equiv C{-}Cl$ is the lowest, and thus the decomposition starts at the tertiary C-atom, giving an IDT close to that of PVC.

The activation energies for various types of C–Cl bonds decomposition are as follows [19]:

	E_a, kcal/mol
CH_3CH_2Cl	60.8
	50.5
	45.0

If these values are compared with the E_a values for CAPP samples (Fig. 4), it can be seen that the maximum E_a of 41.2 kcal/mol occurs at 53.5 wt% chlorine. However, this value is raised to 54.9 kcal/mol if the decomposition is carried out in nitrogen. However, even these values do not reach the E_a for the primary C–Cl bond present in CH_3CH_2Cl. With the increasing degree of chlorination, initially the tertiary, then the secondary, and lastly the primary H-atoms are substituted. This also results in disturbing the structure of the original APP. As progressive chlorination takes place, more and more secondary and primary H-atoms are substituted by chlorine, thus increasing the stability of CAPP. One has to remember that E_a of PVC varies widely (31-41.1 kcal/mol) [20]. However, these values are less than those obtained for CAPP with a chlorine content of more than 42 wt% chlorine. The E_a values in the presence of air are lower than those in nitrogen, due to a faster rate of degradation. Similar results have been obtained for PVC [21].

Figure 5 shows the dependence of char yield (Y_c) at 600°C on both the degree of chlorination and the nature of the atmosphere. It shows that increasing the chlorine content in CAPP, with its decrease in the number of H-atoms, retards the formation of more volatile degraded products, thus resulting in an increase in char yield.

From the preceding discussion it can be inferred that reaction of oxygen during degradation leads to formation of more volatile products like ketones, carboxyl derivatives, hydroperoxides, and peroxides, resulting in a decreasing amount of carbonaceous mass and faster degradation [22].

Differential Thermal Studies

The results in Fig. 6 show that ODT values increase with increasing degree of chlorination, and the curve is similar to that of IDT values obtained from TGA. It appears that reasons similar to those ascribed to the IDT values are also valid here.

Glass Transition Temperature (T_g)

Figure 7 shows that the T_g increases almost linearly with chlorine content up to 35 wt% chlorine and then gradually levels off.

In a completely hydrocarbon polymer, such as APP, the cohesive energy density (CED) is very low, resulting in very flexible chains, and a T_g of -13°C [23]. With the introduction of chlorine there is a gradual change from a nonpolar to polar structure, leading to greater secondary forces between the chains due to dipole-dipole interaction and H-bonding. This, in turn, will lead to an increase in CED as well as in T_g [24]. However, the nature of substitu-

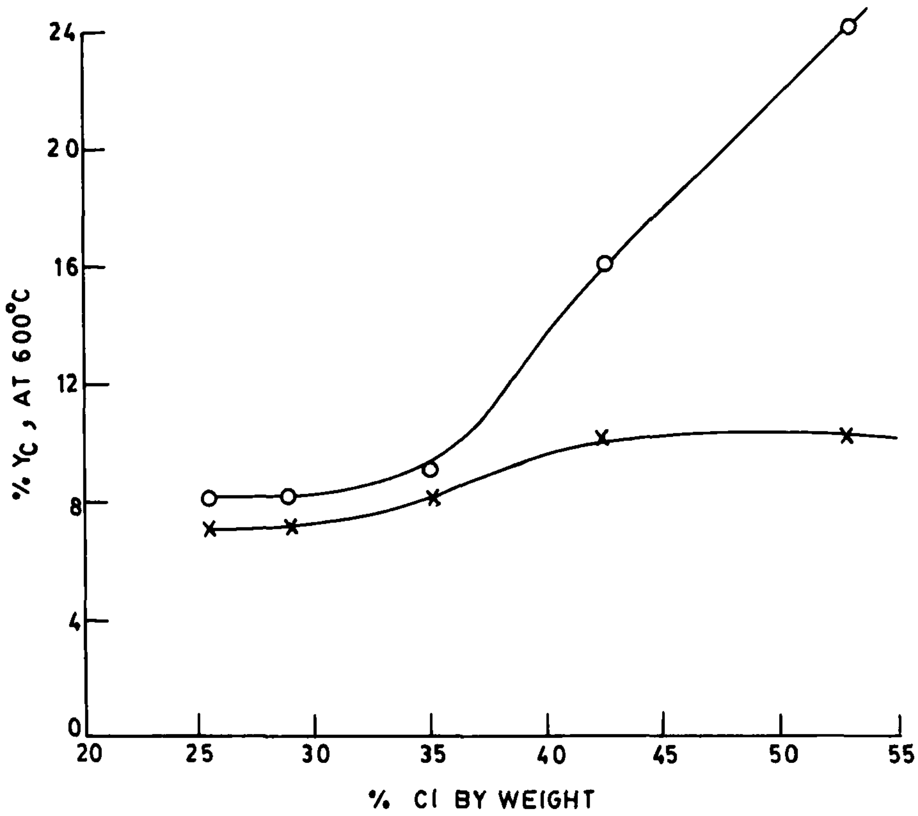


FIG. 5. Variation of Y_c with wt% Cl in CAPP: (○) in nitrogen and (X) in air.

tution plays a major role, e.g., PVC has a T_g of 80°C and PVDC has one of -20°C. This can be explained by the mutual cancellation of dipole moments due to the presence of both chlorine atoms on the same carbon atom but in opposite directions. On the other hand, in the case of CPVC, T_g increases continuously with increasing chlorine content [25]. This may be due to the introduction of a second chlorine atom, generating a new dipole moment whose vector sum exceeds the individual moments [26].

It was reported earlier that introduction of chlorine atoms in APP leads to an increase in the stiffness of the molecular chains, thus restricting free chain movement [27]. It appears that a similar mechanism is also operative here.

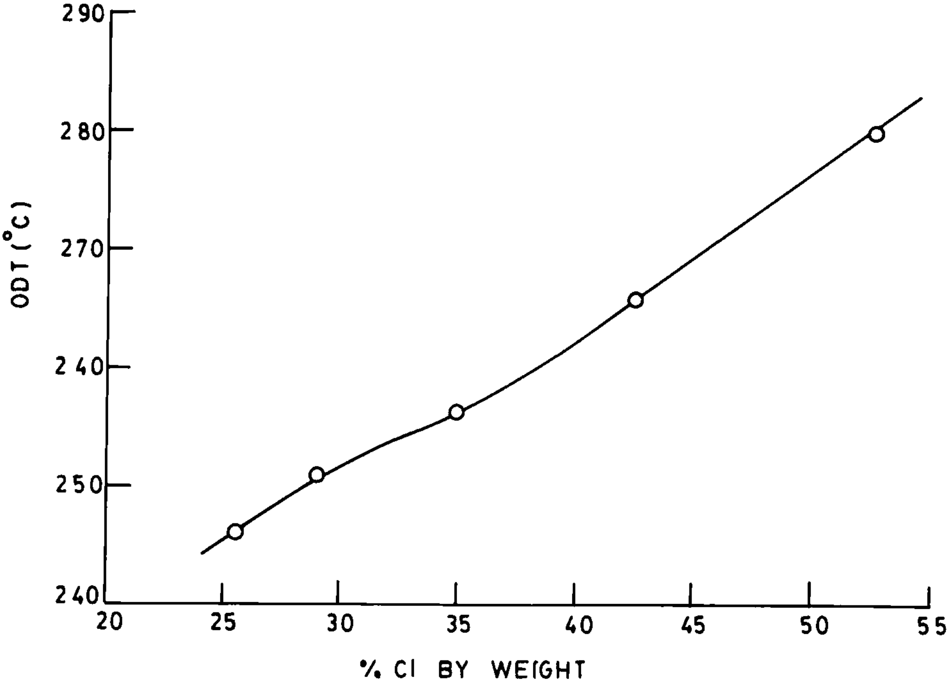


FIG. 6. Variation of ODT with wt% Cl in CAPP.

Polymer Melting Temperature (PMT)

The PMT increases continuously with chlorine content (Table 3). Similar results were also obtained by others [21].

This increase in PMT again can be ascribed to an increase in the CED of CAPP with increasing chlorine content. However, the DTA results indicate that there is a broad range of PMT instead of a sharp melting point. This suggests heterogeneity of chlorine substitution in CAPP since a homogeneous polymer like PVC shows a sharp melting point [28]. But because all types of chlorine atoms (primary, secondary, and tertiary) are present here, no sharp melting point is observed.

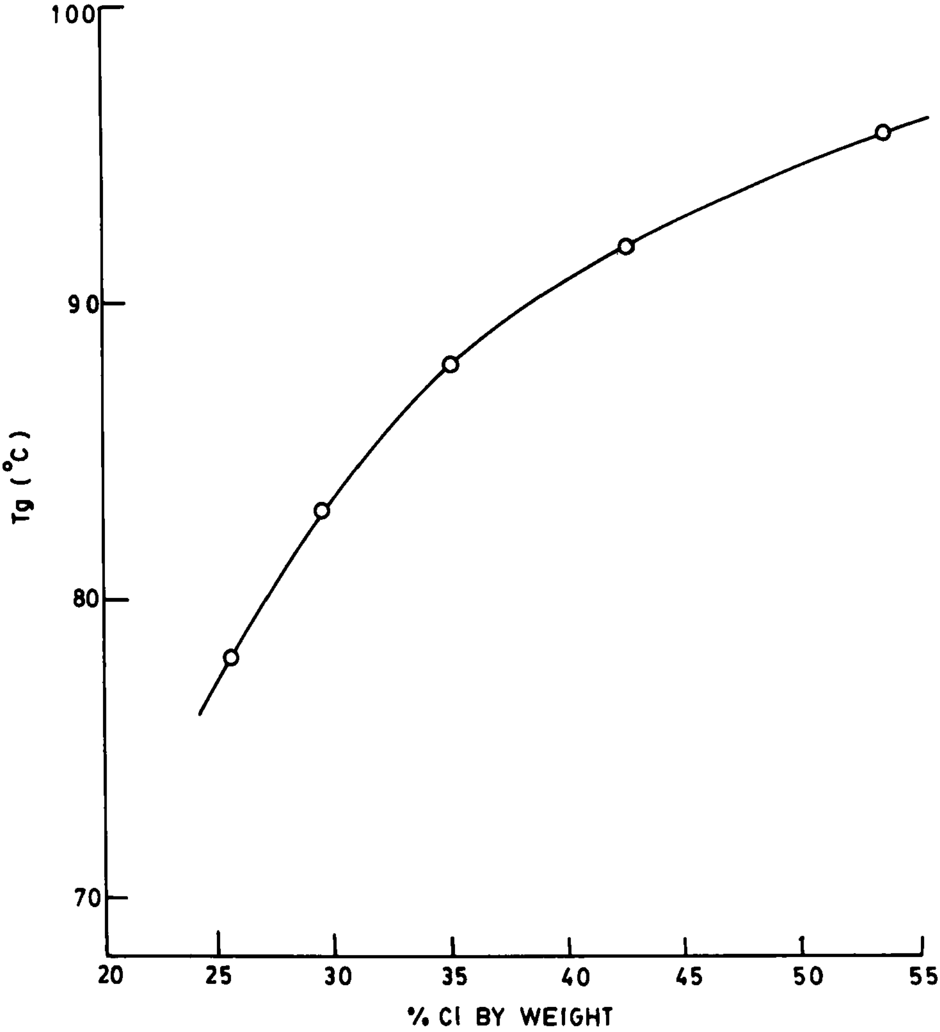


FIG. 7. Variation of T_g with wt% Cl in CAPP.

TABLE 3. Polymer Melting Temperatures of CAPP Samples from DTA Study

	PMT, °C		
Cl, wt%	Range	Average	Peak
25.1	132-197	164.5	172
28.0	162-204	183	199
35.0	132-236	184	187
42.5	184-234	209	228
53.5	204-252	228	239

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