

Chlorinated Atactic Polypropylene as a Plasticizer for Poly(vinyl Chloride)*

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Synopsis

Atactic polypropylene, a byproduct obtained in the manufacture of isotactic polypropylene, has been chlorinated under various reaction conditions. The chlorination reaction is reasonably fast so as to give a product of 53–63% chlorine content in 3 h. The chlorinated product has been incorporated in poly(vinyl chloride) formulations with a view to study its plasticizing activity. Generally this type of compound acts only as a secondary plasticizer; hence it has been used in combination with di(2-ethylhexyl)phthalate, a primary plasticizer. Different proportions of these two plasticizers have been added to poly(vinyl chloride) resin to obtain a series of formulations. These compounds were evaluated, and it appears that the addition of chlorinated atactic polypropylene (APPC) helps in easy processing and increases the throughput. The increasing concentration of APPC showed an upward trend in die head pressure and torque indicating an increase in melt viscosity. The results of physical properties evaluation show that APPC acts as a reinforcing agent and also imparts permanence to the plasticizers.

INTRODUCTION

The use of the conventional Ziegler–Natta catalyst for the production of isotactic polypropylene yields about 10% atactic polypropylene as a byproduct. The major use of this product is in water-proofing compositions,^{1,2} wherein it is mixed with bitumen and other ingredients. A small amount is also used in hot melt adhesives³ and coating material for papers.^{4,5} Still a large amount of it remains unutilized and creates a problem for its disposal, especially by incineration due to high energy costs.

Chlorination of atactic polypropylene has been reported in the literature,^{6,7} and products with various chlorine content have been made. This chlorinated product has a myriad of applications such as surfactants,⁸ bonding of nonwoven fabric,⁹ sizing of polypropylene yarn,¹⁰ fire-retardant adhesives,¹¹ lube oil additives,¹² and in printing ink formulations.¹³

We have attempted to utilize chlorinated atactic polypropylene as a secondary plasticizer for poly(vinyl chloride) resins. Chlorination has been carried out under various conditions so as to obtain a range of chlorine content in the product. The effect of various catalyst systems, sunlight, and ultraviolet (UV) light has been studied.

The commonly used secondary plasticizers for poly(vinyl chloride) resins are epoxidized vegetable oils and chlorinated paraffins. These substances do help in easy processing of resins and make the product flexible. We have incorporated chlorinated atactic polypropylene along with dioctyl phthalate in poly(vinyl chloride) (PVC) formulations in various proportions. The results indicate that

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this product helps in easy processing of PVC compounds as well as imparting reinforcing characteristics and permanence of plasticizers.

EXPERIMENTAL

Atactic Polypropylene (APP)

The APP used was obtained from our isotactic polypropylene (Koylene brand) plant and has the following characteristics; \bar{M}_n 1057 and melting range of 98–102° C. The product as such has about 4% moisture and 5% heptane. The APP was purified by refluxing with methanol in an Soxhlet apparatus and drying in a forced air drier at 45° C. The dried product was a white rubberlike solid.

Poly(vinyl Chloride) (PVC)

Suspension grade PVC resin of DP 1000 was used in this investigation. It was obtained from Messrs. National Organic Chemical Industries, Ltd., Bombay.

Chlorination of Atactic Polypropylene (APPC)

Chlorination of purified, dried APP was carried out in CCl_4 solution with and without catalysts and in presence of UV light or natural light (Table I) at room temperature. The product obtained was analyzed for chlorine content, unsaturation (dehydrochlorination reaction), and melting point. No unsaturation could be detected in APPC as shown by a zero bromine number. Its melting point depends upon chlorine content: however, it is not sharp and the product of 55–60% chlorine content melts in the range of 115–120° C.

TABLE I
Reaction Conditions for Chlorination of Atactic Polypropylene^a

Sample no.	Catalyst/inhibitor	Irradiation conditions	Reaction time, h	Chlorine content, %
1	Bz ^b	Sunlight	3	59.7
2	Bz ^b	UV lamp, 300 W	3	58.9
3	AIBN ^b	Sunlight	3	57.3
4	LPO ^b	Sunlight	3	53.1
5	—	Sunlight	2	46.6
6	—	Sunlight	3	53.8
7	—	Sunlight	4	55.2
8 ^c	—	Sunlight	3	62.6
9 ^c	—	Sunlight	4	63.0
10	—	Dark	3	39.9
11	HQ ^b	Sunlight	3	44.5

^a APP = 100 g, CCl_4 = 500 mL, catalyst/inhibitor = 0.5 g.

^b Bz = benzophenone, AIBN = azobisisobutyronitrile, LPO = Lauryl peroxide, and HQ = hydroquinone.

^c CCl_4 = 1000 mL.

Compounding and Preparation of Samples

Compounding of chlorinated APP with PVC and other ingredients was carried out using the Planetari mixer of a Brabender Plasticorder at 100° C. A typical formulation is given below:

- (1) poly(vinyl chloride) resin—100.0 g;
- (2) dioctyl phthalate—25.0 g;
- (3) chlorinated APP—25.0 g;
- (4) tin stabilizer—3.0 g;
- (5) stearic acid—0.5 g;
- (6) calcium stearate—0.5 g;
- (7) cetyl alcohol—0.5 g.

Poly(vinyl chloride) compound thus obtained was a free-flowing material and its processing characteristics were tested on a single screw extruder L/D 25 of Brabender Plasticorder with a 1-mm die of L/D 15 and entry angle of 60°. The extruder has attachments for recording torque and die-head pressure. Throughput of the compound was determined by weighing the material extruded in 10 min at a fixed rpm and constant temperature profile of the extruder barrel. The effect of chlorinated APP on processing characteristics is shown in Table II.

For making test samples for physical properties determination, the remaining free-flowing powder was extruded through another single screw extruder of L/D 20 and a rod die of 4-mm diameter. The strands were quenched in water and pelletized. These pellets were compression molded into 3-mm thick sheets at 165° C and 50 kg/cm² pressure and then cut into samples of desired specifications. The samples were tested for tensile strength, percent elongation, hardness (Shore D), haze, gloss, and permanence of plasticizers according to ASTM methods.

RESULTS AND DISCUSSION

Chlorination of APP was carried out at room temperature, and the effect of catalyst, sunlight, solvent concentration, UV light, and UV sensitizers was studied. In all these experiments the rate of chlorine inlet was kept constant and the extent of chlorination was estimated by determining chlorine content by the Parr Bomb fusion method. It is seen from Table I that the chlorination reaction is sufficiently fast, showing chlorine contents between 53% and 63% in about 3 h. Omichi and co-workers¹⁴ have established that chlorination of APP under γ radiation proceeds through a free radical mechanism. Our observations as indicated in Table I prove that chlorination even in sunlight proceeds through radical mechanism, because the rate of reaction becomes slow when the reaction is carried out in the dark. Chlorination reaction in sunlight is very fast in the first 3 h and then proceeds slowly. Addition of UV sensitizers like benzophenone slightly accelerates the rate whereas free radical sources like azobisisobutyronitrile (AIBN) and lauryl peroxide do not affect the rate of chlorination to an appreciable extent because of lower reaction temperature. Addition of inhibitor like hydroquinone retards the rate of chlorination. Infrared (IR) spectra of both APP and APPC in CCl₄ solutions were recorded on a Perkin-Elmer infrared spectrophotometer model 567. IR spectra of APP and APPC are shown in Figure 1. The spectrum of APPC has additional bands at 630, 703, 724, 815, 1010, 1260, 1300, and 1390 cm⁻¹. IR absorption at 724 and 703 cm⁻¹ are assigned to C—Cl stretching vibrations. ¹³C-NMR spectra of APPC (62.6% chlorine) and APP are shown in Figure 2. The spectra were recorded on a JEOL FX-100 NMR

TABLE II
Effect of Chlorinated APP on Processing Characteristics of PVC^a

Sample no.	Plasticizer composition, phr		Die-head pressure P , kg/cm ²	Torque, T , m g	Throughput		
	Total	APP			Q , g/10 min	P/Q	T/Q
1	25	0.0	319.8	3300-3350	115.4	2.77	28.59
2	50	0.0	91.3	875-900	128.9	0.70	6.78
3	50	12.5	231.0	2000-2025	119.5	1.93	16.73
4	50	18.8	108.0	750-775	84.0	1.05	8.86
5	50	25.0	239.7	1950-2000	103.8	2.30	18.78
6	50	37.5	263.6	2500-2550	140.2	1.88	17.83

^a rpm = 20, extruder $L/D = 25$; die diam = 1 mm; die $L/D = 15$. Temperature, °C: zone 1 = 150; zone 2 = 155; zone 3 = 162; die = 162.

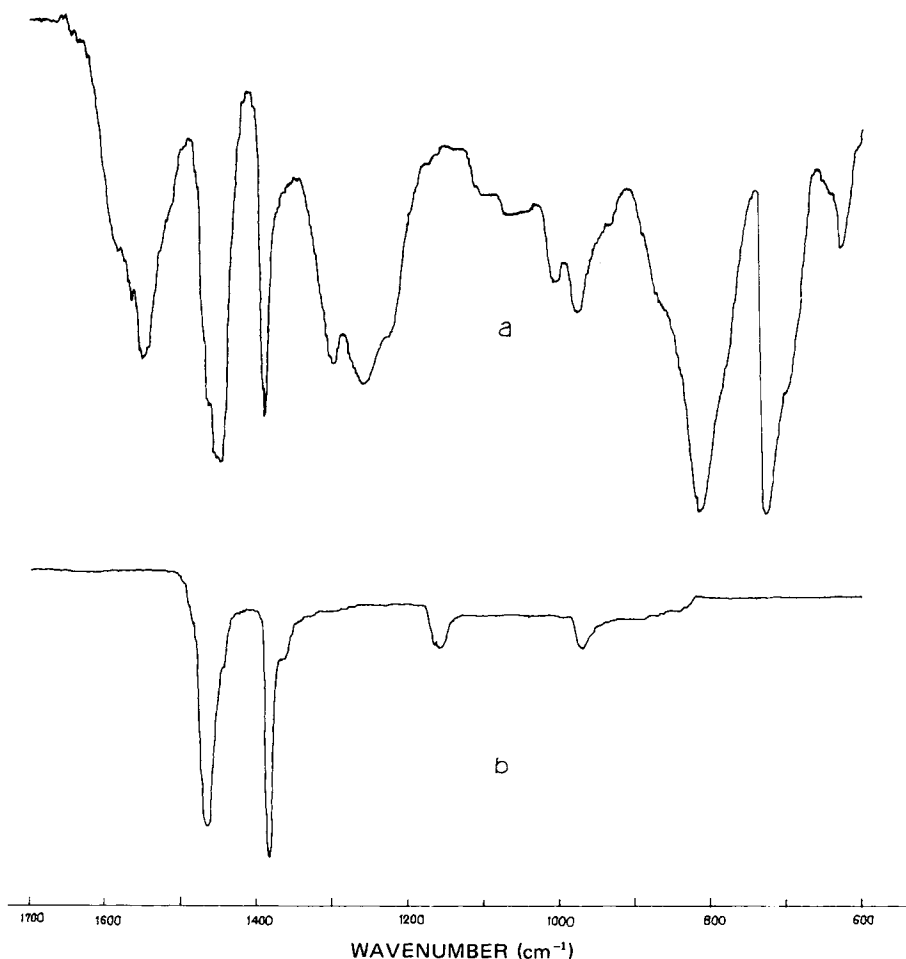


Fig. 1. IR spectra of (a) chlorinated atactic polypropylene and (b) atactic polypropylene.

spectrometer. As shown in the figure, all carbons in APPC shifted downfield due to incorporation of chlorine into the monomer unit. The absorptions obtained are centered at 101.7, 74.2, 64.6, 47.3, 44.8, 41.6, 28.8, and 12.1 ppm. From the spectrum it can be interpreted that chlorine is distributed to all the carbon atoms. Lowest field absorption at 101.7 ppm is probably due to CCl_3 carbon, thereby indicating trihalogenation at CH_3 . The absorptions at 74.2 ppm and 64.6 ppm may be ascribed to tertiary carbon attached to chlorine and CHCl carbons, respectively. Absorption at 44.8 and 41.6 ppm are supposedly due to the CH_2Cl carbon. The broad absorptions obtained are due to many configurational possibilities associated with APPC. The detailed ^{13}C analysis will be communicated separately.

Polymeric plasticizers for PVC have gained considerable importance because of their permanence in the PVC compounds. Their resistance to extraction from the compounds opens new applications such as petrol hoses, hospital sheeting, and protective clothings. Blending of APPC with PVC proceeded smoothly at a temperature of 100°C ; below this temperature APPC did not mix fully with the resin, and extrusion of the mix became difficult. Secondary plasticizers are

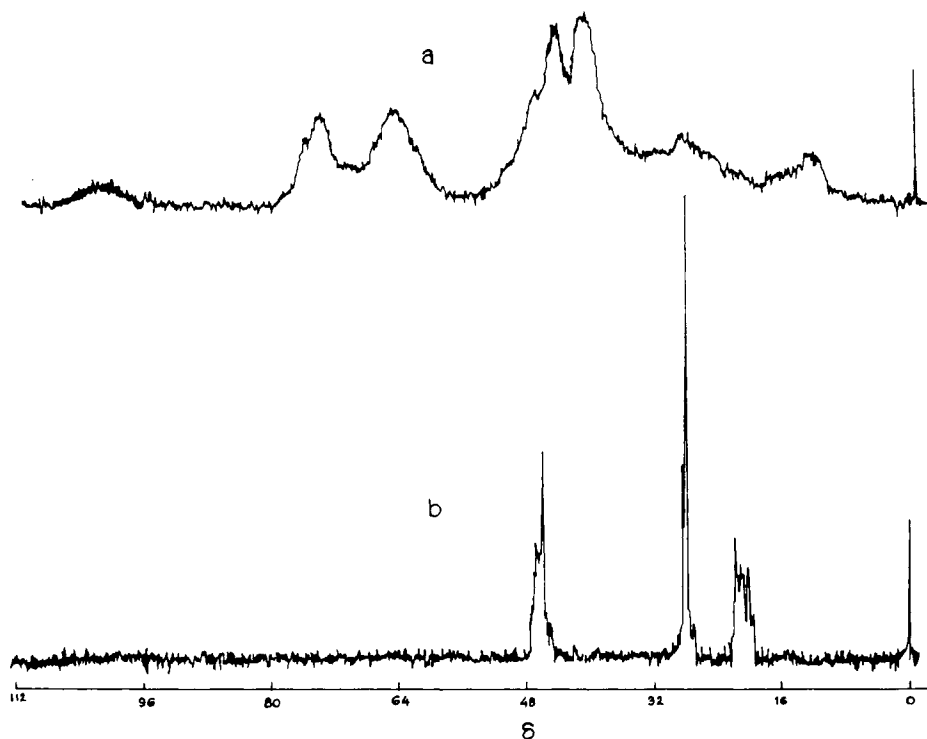


Fig. 2. 25 MHz ^{13}C -NMR spectra of (a) chlorinated atactic polypropylene and (b) atactic polypropylene at 50°C in C_6D_6 .

never used alone in PVC formulations. The most commonly used primary plasticizer along with the secondary is di(2-ethylhexyl)phthalate, generally named as dioctylphthalate (DOP). The various formulations of PVC containing different proportions of APPC and DOP were mixed in a Planetari mixer, keeping total concentration of primary and secondary plasticizer constant at 50 parts per hundred resin (phr). The free flowing PVC compounds thus obtained were extruded through a single screw extruder at a fixed rpm and temperature profile of the barrel with a view to study the plasticizing effect of APPC on PVC. Plasticizers generally help in ease of processing of PVC, and this is evident from Table II wherein throughput, torque, and die-head pressure of various formulations are given. There is an improvement in throughput with increasing concentration of APPC; however, both die-head pressure and torque have registered an upward trend. This seems to be due to the rise in melt viscosity of the compound. All the values reported agree, within the limits of experimental error, except the formulation containing 31.2 phr of DOP and 18.8 phr of APPC. Exceptional low torque, die-head pressure, and throughput can be attributed to high slippage in the extruder barrel. However, we are looking for possible reasons of high slippage only in this formulation.

Plasticizers greatly affect the mechanical properties of the resins, and there is almost a linear relationship between reduction in mechanical properties with

TABLE III
Effect of Secondary Plasticizer on Mechanical Properties of PVC

Sample no.	Plasticizer composition, phr		Tensile strength, kg/cm ²	Elongation, %	Impact strength, kg-cm/cm	Hardness, shore, D
	DOP	APPC				
1	25.0	—	195.0	192.0	flexible	60
2	50.0	—	148.4	456.3	flexible	30
3	37.5	12.5	198.0	376.0	flexible	45
4	31.2	18.8	184.5	298.3	flexible	53
5	25.0	25.0	218.0	214.0	3.71	68
6	12.5	37.5	387.6	5.2	2.34	78

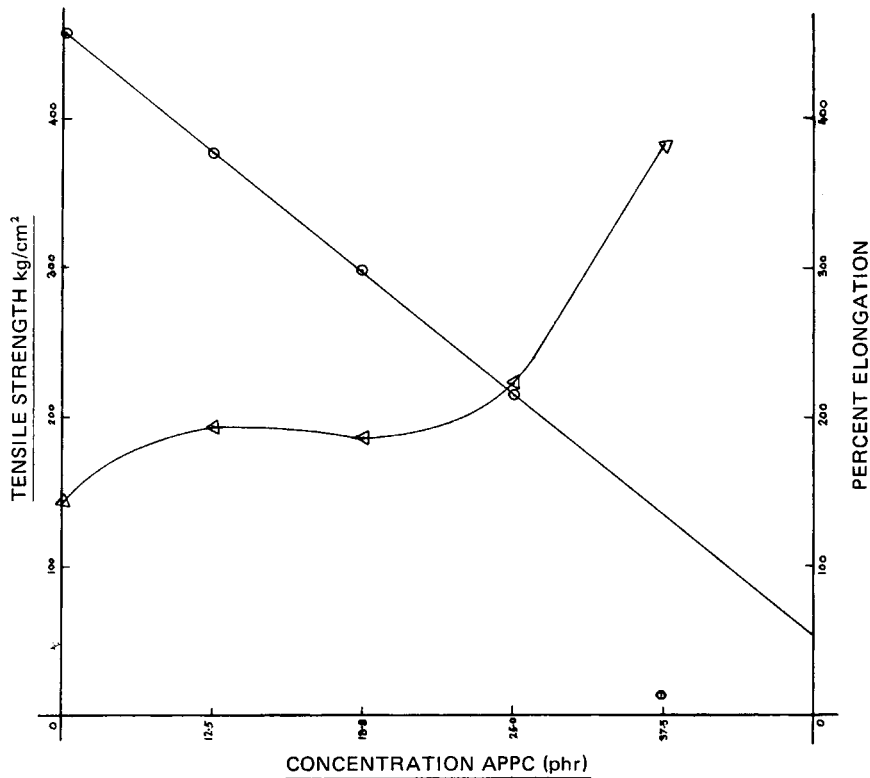


Fig. 3. Tensile strength and percent elongation versus concentration of APPC (phr): (Δ) tensile strength, (○) % elongation.

increase in plasticizer concentration. It can be seen from Table III that the increase of DOP from 25 to 50 phr has resulted in a 137.6% increase in elongation, 23.9% decrease in tensile strength, and a 50% fall in hardness. The incorporation of APPC along with DOP has resulted in an increase of tensile strength and hardness, but elongation has been reduced (Fig. 3), thus indicating reinforcing characteristics of APPC. In the case of mechanical properties the exception has again been the formulation containing 31.2 phr and 18.8 phr of DOP and APPC,

TABLE IV
Effect of Secondary Plasticizer on Optical Properties of PVC

Sample no.	Plasticizer composition, phr		Haze, %	Gloss, %
	DOP	APPC		
1	25.0	—	16.0	108.6
2	50.0	—	18.7	101.5
3	37.5	12.5	20.0	95.6
4	31.2	18.8	43.3	81.8
5	25.0	25.0	56.2	86.6
6	12.5	37.5	—	89.3

TABLE V
Migration of Additives in PVC

Sample no.	Plasticizer composition, phr		Hexane, %	Mineral oil, %	2% soap solution
	DOP	APPC			
1	25.0	0.0	2.07	nil	nil
2	50.0	0.0	21.10	2.77	1.13
3	37.5	12.5	4.43	nil	nil
4	31.2	18.8	0.70	nil	nil
5	25.0	25.0	nil	nil	nil
6	12.5	37.5	nil	nil	nil

respectively. The hardness and elongation results show the expected trend, i.e., an increase but tensile strength shows a downward trend.

It is well known that addition of secondary plasticizers to PVC formulations leads to slightly hazy products. The data given in Table IV show that formulation containing 37.5 phr of APPC is so hazy that it was not possible to record its value on a Gardner gloss and haze meter. The decrease in gloss values was not very pronounced; however, gloss of the samples decreased with increasing concentration of APPC in the formulations.

Permanence of plasticizers in PVC compounds, which is an inherent property of polymeric plasticizers, was also investigated. The various solvents examined were *n*-hexane, mineral oil (Enklo-44 of M/s. Hindustan Petroleum Corporation, Bombay) and 2% aqueous solution of Idipol (detergent from M/s. Indian Drugs and Pharmaceuticals Ltd., Hyderabad). The extractions were carried out at room temperature for 48 h. The results described in Table V show that there is virtually no loss of additives when APPC was added to the formulations. Without APPC, hexane was able to extract more than 20% of the additives, mineral oil, 2.7%, and soap solution, 1.1%, from PVC formulations containing 50 phr of DOP.

From the results obtained it is very clear that the addition of APPC in PVC formulations helps in easy processing, increases tensile strength and hardness, but lowers percent elongation and optical properties. The migration of plasticizers from PVC compounds in contact with solvents like hexane, mineral oil, and soap solutions is reduced to a very large extent on addition of APPC.

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