Journals Pub

International Journal of
Polymer Science & Engineering

ISSN: 2455-8745
Volume 11, Issue 1, 2025
January–June
DOI (Journal): 10.37628/IJPSE

https://journalspub.com/journal/ijpse/

Research IJPSE

Novel Process for the Synthesis of Chlorinated Polyvinyl Chloride Using Unsaturated Polyvinyl Chloride Resin

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Abstract

The present work relates to the process for synthesizing reactor-made chlorinated polyvinyl chloride (CPVC) from commercially available thermally treated unsaturated PVC. The synthesis of CPVC is a two-step process. The first step involves the controlled thermal treatment of PVC to generate unsaturation in the PVC chain. The second step is the chlorination of the thermally treated PVC in the presence of an initiator and water as the dispersion medium. Maximum chlorination is achieved in 4 hours of reaction time, with 68% chlorine content in the PVC. The physical properties of the CPVC resin were evaluated and found to be comparable with commercial CPVC resin. SEM images showed very good morphology of the CPVC resin without agglomeration of the particles. The chlorination process can be conducted in suspension/dispersion mode or in solution, each method offering unique benefits for process control and the qualities of the finished product. The produced CPVC demonstrated improved physical properties, chemical resistance, and thermal stability, qualifying it for use in industrial settings for coatings, fittings, and pipe production. This study offers a very unique and economical method to produce CPVC.

Keywords: Polyvinyl chloride, chlorination, dehydrochlorination, unsaturation, chlorine content

INTRODUCTION

Polyvinyl chloride (PVC) is the utmost popular thermoplastic polymer globally. However, its softening temperature is around 65–75°C, which severely limits its application at temperatures higher than 65°C. If the chlorine content of PVC can be elevated to more than 0.65 g . g – 1 (>65%) by chlorinating it to chlorinated polyvinyl chloride (CPVC), the softening temperature will exceed 100 °C and its application will be widely broadened. Benefiting from its strong mechanical properties, flame-retardant ability, and acid- and base-proof character, CPVC has been one of the high-performance thermoplastics and used as engineering plastics. CPVC application covers fire water sprinklers, joints-elbow, windows panels, hot water pipes, and fittings [1]. The CPVC is conventionally synthesized by following three common methods, i.e., gas-solid method, solvent method, and aqueous suspension process but among these solid and aqueous suspension methods are commercially viable. The aqueous suspension method brings severe environmental concern for discharged waste liquid, harmful gases, and corrosion of equipment surfaces due to moist chlorine gas. In compression, a gas sloid method is a better process. The main challenges of this process are to find an effective initiator for greater yield and better product quality. UV, LED, plasma treatment, and X-ray irradiation are also used for the generation of the free radical in the PVC chain in the gas-solid process [2]. Three parameters were studied to understand the

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Received Date: January 06, 2025
Accepted Date: January 30, 2025
Published Date: February 10, 2025

Citation: Saurabh K. Tiwari, Virendra Kumar Gupta. Novel Process for the Synthesis of Chlorinated Polyvinyl Chloride Using Unsaturated Polyvinyl Chloride Resin. International Journal of Polymer Science & Engineering. 2025; 11(1): 14–23p.

chlorination process of CPVC and found that temperature is the most sensitive factor in the PVC chlorination process along with chlorine concentration and UV intensity. The high solubility of chlorinated PVC in respective solvents makes it more suitable for adhesive and fiber applications. For this reason, the radiation-induced solution chlorination of PVC in methylene chloride was studied. Chlorine reacted with PVC in the methylene chloride solvent and chlorinated in a very small percentage to chloroform and tetrachloromethane as side products [3–6]. Chlorine content depends upon UV initiator intensity, chlorination time, reaction temperature, and pressure. This chlorine content of CPVC affects the density as well as the volume expansion and diameter expansion of CPVC products [7]. Lu et al. (2011) used a circulating fluidized bed to synthesize chlorinated PVC in a two-step process. They achieved 65% chlorine content with uniform chlorine distribution inside the particles and a fine microstructure [8].

In the present work, a novel approach has been adopted to synthesize chlorinated PVC that employed an aqueous suspension method and unsaturated PVC resin. Chlorinated PVC was synthesized by chlorination of thermally treated unsaturated PVC resin in presence of a catalyst.

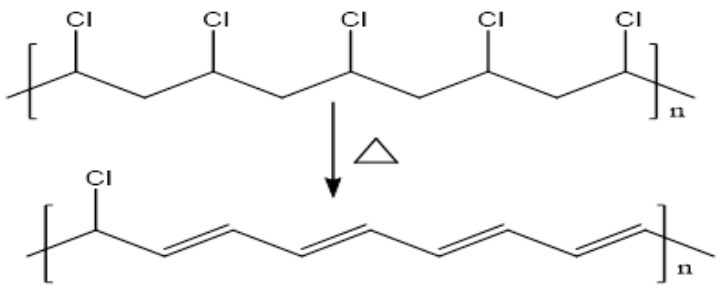
MATERIALS AND METHODS

K67-11 grade of PVC resin from Reliance Industries Limited and 50% concentrated H_2O_2 from SD Fines were used. Sodium hydroxide with a 99.99% purity level was taken from SD Fines and used for neutralizing the pH of the solid cake. Differential Scanning Calorimetry (DSC-Q2000, TA instruments) characterization tool used to understand the thermal behavior of CPVC resin. TGA analysis is done in Nitrogen atmosphere and 10°C/min heating rate. The morphology of CPVC resin was investigated by Scanning Electron Microscopy (SEM) (FEI-NOVA NANOSEM 650). The chlorine content of CPVC resin was evaluated using 13C NMR (Bruker Avance III HD-400 MHz). Unsaturation in PVC resin was evaluated with help of a UV instrument (Shimadzu UV-1780). Particle size analysis was done using CILAS 1090 particle size analyzer.

Dehydrochlorination of PVC

The highly unsaturated PVC is synthesized by controlled thermal treatment of the PVC resin in the temperature range of 170–200ºC in a vacuum oven. The commercially available PVC resin normally contains chlorine content of up to 55–56%. Thermal degradation of PVC involves free radicals, which generates new labile defects in PVC chain and leads to auto acceleration of HCl loss, resulted double bond in PVC backbone [9]. Upon the controlled thermal treatment, the liberation of hydrochloric acid (HCl) takes place and generates the double bonds in the PVC chain as shown in Scheme-1 and making the pink-brown colored product. This color generation is due to the generation of unsaturation in the PVC backbone.

The liberation of the HCl also increases as the temperature increases, resulting in the formation of color (pink-brown) in resin from white PVC resin. This pink-brown colored PVC is washed with DM water and dried under a vacuum oven at 60°C for 4 hrs to get rid of the trapped HCl in pores during the thermal treatment.



Scheme 1. Thermal treatment mechanism of PVC.

Polyene concentration of thermally treated PVC at different temperatures was evaluated. Polyene concentration was calculated using UV spectra as reported by Tibor Szakacs and Bela Ivan, 2004 [10]. The polyene concentration was evaluated using the correlation given in Equations (1) & (2).

$$\text{Concentration of Polyenes(pi)} = A*M/\epsilon*C*d \quad (1)$$

M = molecular weight of PVC
ϵ = Absorption coefficient
C = polymer concentration in g/dm^3
d = optical path length
A = absorbance

$$\varepsilon_{i,THF} = 10000 + 27700 \times (i - 1)\ (dm^3\ mol^{-1}cm^{-1}) \quad (2)$$

ε = Absorption coefficient
i = Polyene length

Absorption spectra of thermally treated PVC resin (D-PVC) at 170°C, 190°C, and 200°C were recorded using UV instrument by dissolving 20 mg D-PVC in 3 ml of tetrahydrofuran (concentration will be approx. 0.1 molar). A highly concentrated solution is needed because of the low absorbance of thermally treated PVC between 300 and 600 nm wavelength ranges. Absorbance peaks were found in the wavelength range 250–460 nm as showed in Figure 1(a).

Using Equation (2) the polyene length was calculated and for every polyene length corresponding wavelength (nm) maximum was taken as shown in Table 1. Further polyene concentration was calculated using Equation (1).

Table 1. Polyene length corresponding to wavelength (nm) maxima.

Lamda max	455.5	436	411.5	387.5	363	338	322	309	275
Polyene length (i)	10	9	8	7	6	5	5	4	3

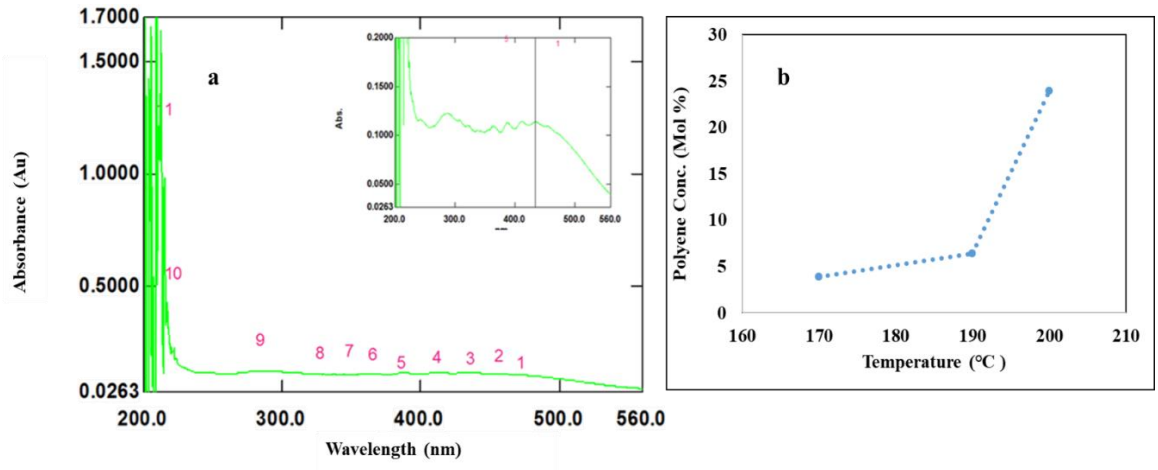
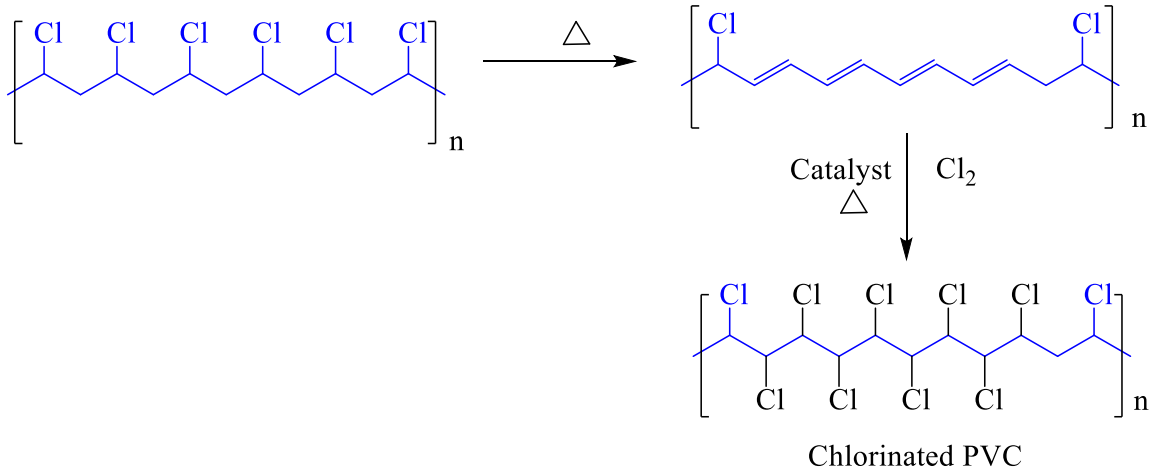


Figure 1. (a) UV spectra of thermally treated PVC at 190°C for 30 min. (b) polyene concentration of thermally treated PVC at different temperatures for 30 min.

The polyene concentration increased with increasing thermal treatment temperatures 170°C, 190°C, and 200°C for a fixed time interval of 30 min as shown in Figure 1(b). Polyene concentration was found 6.5 mol% in thermally treated PVC at 190°C for 30 min in a static oven which was further used as a precursor for the chlorination of PVC.

Synthesis of Chlorinated PVC

An amount of 2 liter pressure glass reactor was used for the chlorination reaction of PVC as showed in Figure 2. Chlorine gas was taken directly from the cylinder. Thermally treated unsaturated PVC resin was used for the chlorination of PVC. The reaction mechanism of unsaturated PVC and chlorine is given in Scheme 2. The chemicals used for the PVC chlorination reaction process are given in Table 2.



Scheme 2. Synthesis mechanism of chlorinated PVC.

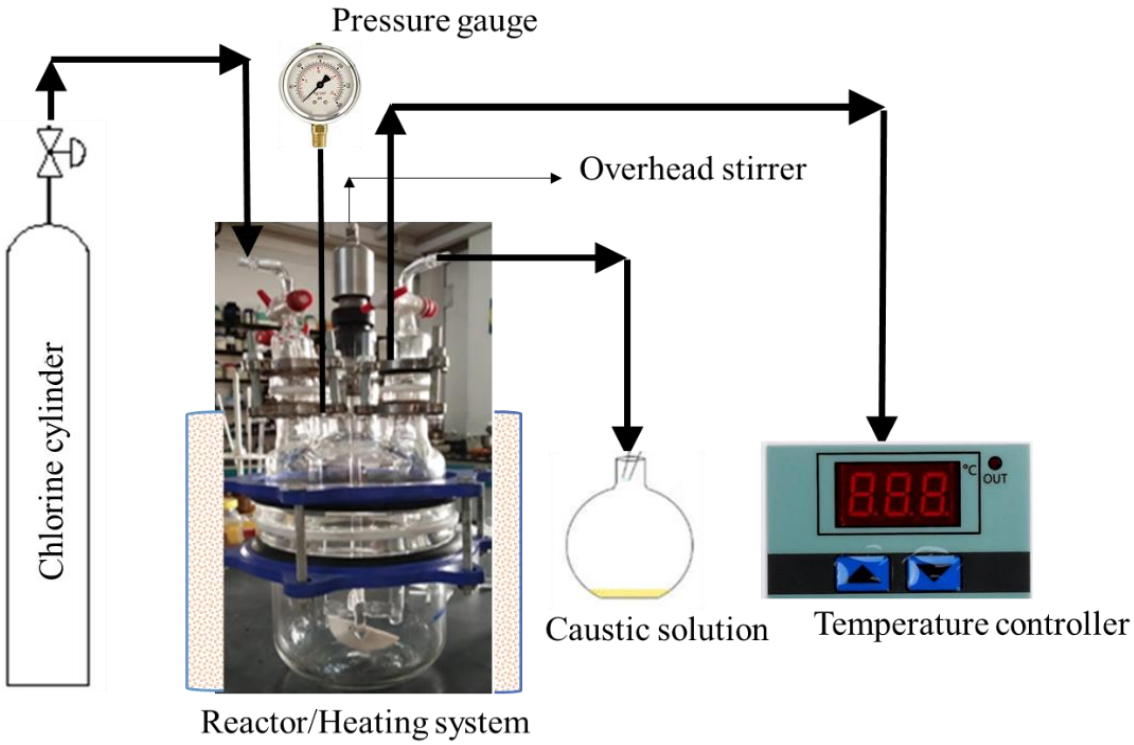


Figure 2. CPVC synthesis process.

The glass reactor was dried completely and purged with nitrogen gas before charging the ingredients. The thermally treated 200 gm PVC resin is taken in 1400 ml DM water in a glass reactor and set the water bath temperature to 85°C. After reaching the reactor temperature to 60°C, added 2% hydrogen peroxide into the solution with respect to the weight of the PVC resin. Charged 2 bar chlorine gas in 2 liter glass reactor. Chlorine gas was charged approximately 6 times during the

reaction (once consumed completely and pressure shows zero in the reactor). Reaction temperature maintained at 85°C for the next 4 hours at 450 rpm stirring speed. The reaction mass showed a distinct color change from dark pink to white which indicates reaction progress. After 4 hours, cool the reaction mass and filter it, and washed first with DM water (3 times) and then with 3% alkali solution to get neutralized pH value of the solid cake. After getting neutralized pH of the solid cake, it is washed with methanol and dry it at 50°C for 5 hours.

Table 2. Chemicals are used for the chlorination of thermally treated PVC resin.

S.N.	Chemicals	Quantity
1	Thermally treated PVC resin	200 gm
2	DM water	1400 ml
3	H_2O_2 (50% Conc.)	2%
4	Chlorine gas produced	2 bar pressure
5	Sodium hydroxide (NaOH) solution (3% solution)	500 ml
6	Methanol	500 ml for washing

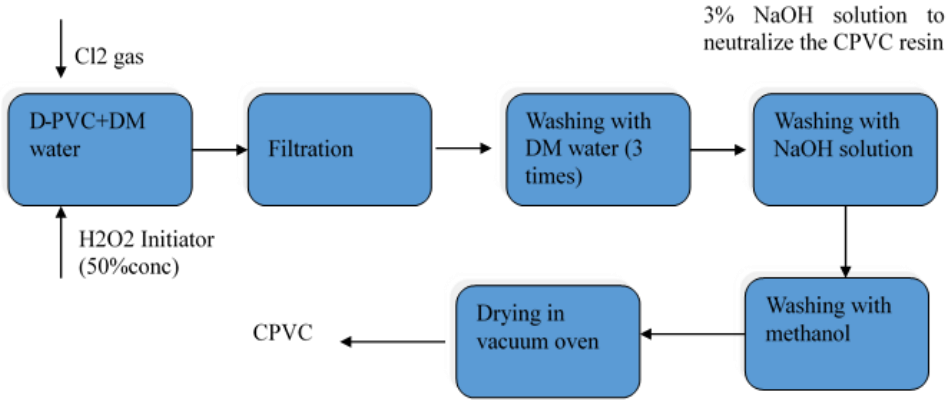


Figure 3. CPVC synthesis process flow chart.

The process flow diagram is given below in Figure 3. 2wt% benzoyl peroxide was used in the CP06 batch as an initiator. In the rest of the batches, 2 wt% H_2O_2 (50% conc.) is used as an initiator.

RESULTS AND DISCUSSIONS

Chlorinated PVC resin was synthesized using free radical polymerization and characterized the physical properties using different analytical tools. The physical properties, like bulk density, average particle size, and porosity of chlorinated PVC resin, were evaluated and mentioned in Table 3.

Table 3. Physical properties of CPVC resin synthesized in different batches.

Samples	Porosity (ml/gm)	Avg. Particle Size (µm)	Bulk Density (gm/ml)
CP06	0.29	127	0.61
CP07	0.26	134	0.48
CP08	0.27	133	0.47
CP09	0.30	135	0.47
CP10	0.31	136	0.46
CP11	0.25	131	0.51
CPS (Commercial CPVC resin)	0.26	136	0.61

Porosity, average particle size, and bulk density were found comparable with commercially available chlorinated PVC resin as mentioned in Table 3. In the chlorination process of PVC, $–CH_2–$ and –CHCl– groups in PVC chain are partly transformed to –CHCl– and $–CCl_2–$ via substitution of

hydrogen by chlorine atoms. The chlorine content was calculated from the spectra of solid 13C NMR using Equation (3) where A is the integrated area for corresponding peaks. 13C NMR represents an increase in the peak intensity of CH–Cl, C–Cl_2 carbon atom related to peaks 55 ppm and 87.5–88.5 ppm respectively which shows significant enhancement in chlorine content. Chlorine content was determined by 13C NMR and found in the range of 64–68%, whereas commercial chlorinated PVC showed 69% chlorine content in CPVC resin [11, 12].

$$f_{NMR} = \frac{(35.5\ A_{-CHCl-} + 71.0\ A_{-CCl2-})}{(48.5\ A_{-CHCl-} + 83.0A_{-CCl2-} + 14.0A_{-CH2-})} \quad (3)$$

The 13C NMR spectra and chlorine content of CPVC, PVC, and commercial CPVC are given below in Figures 4 and 5, respectively. Synthesized CPVC resin showed comparable chlorine content as commercial CPVC. CPVC chlorine content was found in the range of 64–68% as shown in Figure 5. Thermogravimetric analysis (TGA) of CPVC resin was studied in detail and compared to commercial CPVC resin as shown in Figure 6. The thermal stability of CP06, CP07, and CP08 was stable to 265°C. It is slightly lower than the commercial CPVC resin (CPS) may be due to slight difference in chlorine content and after 265°C temperature all three started decomposing due to dehydrochlorination reaction. In the temperature range of 370–800°C, the remaining dehydrochlorination reaction occurred, which resulted in gradual weight loss. This pattern was found similar for all CPVC samples. All the CPVC samples showed approximately 25–27 wt% carbon char yield at 800°C.

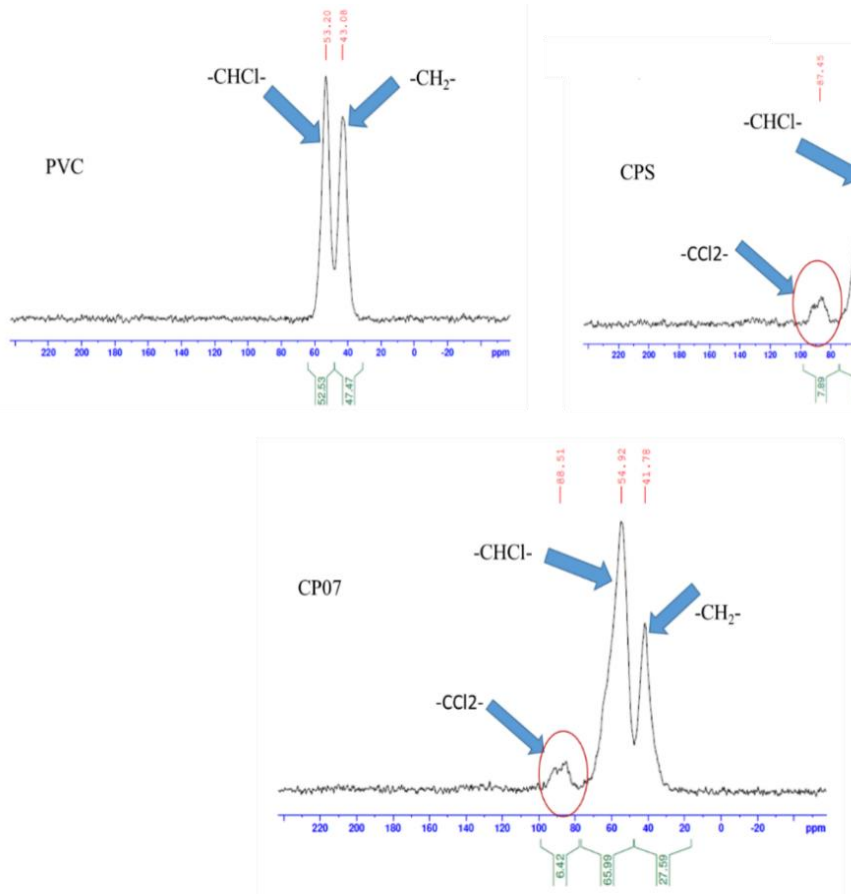


Figure 4. 13C NMR spectra of CPVC & PVC resin.

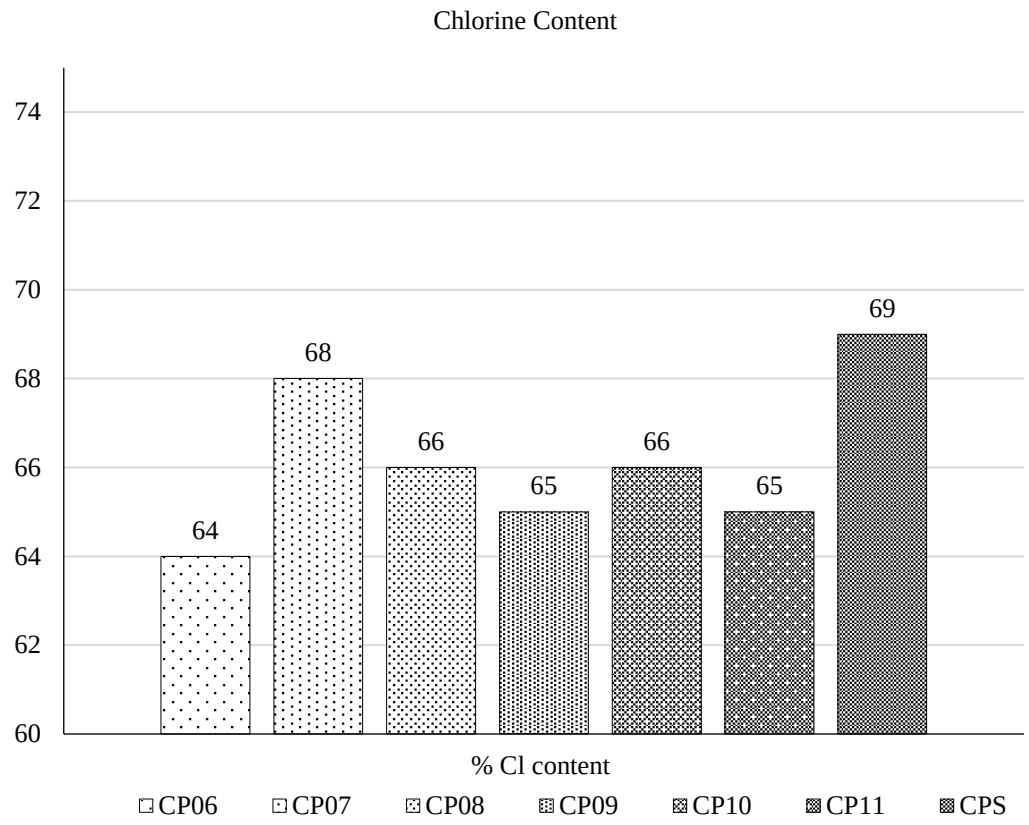


Figure 5. Chlorine % in synthesized CPVC resin.

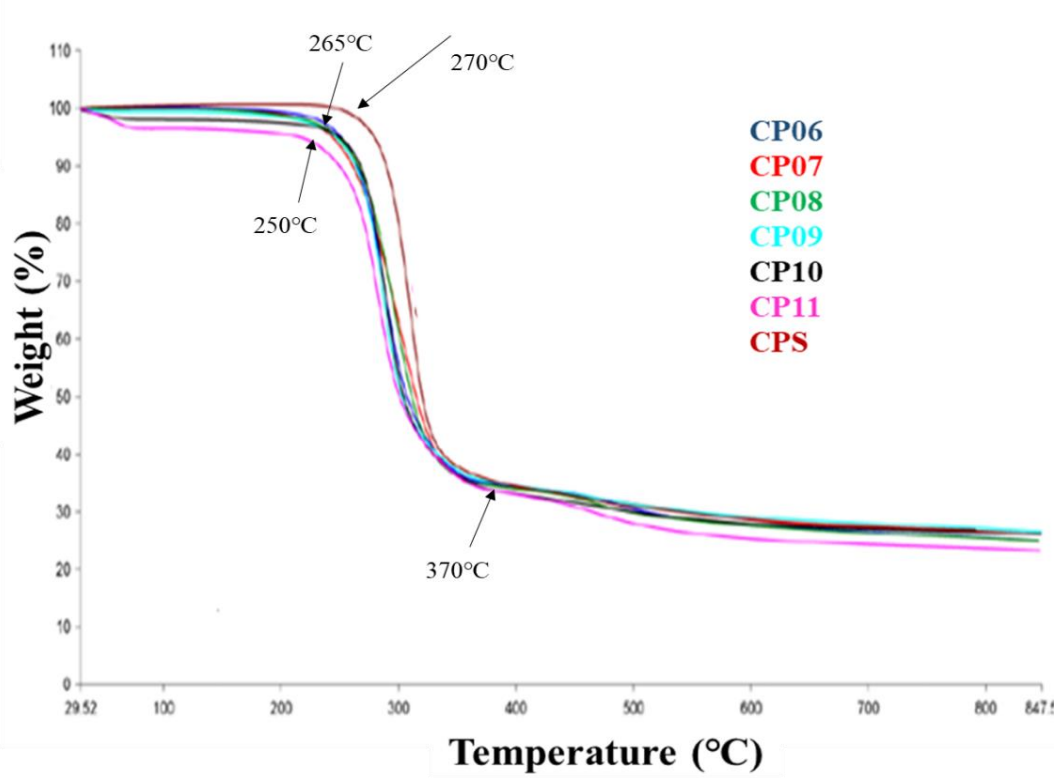


Figure 6. Thermogravimetric analysis of CPVC resin.

The morphology of synthesized chlorinated PVC, PVC, and commercial or standard CPVC resin was studied using Scanning Electron Microscopy (SEM). The morphology of CPVC resin was found almost like PVC and commercial CPVC resin as shown in Figure 7. These CPVC resin particles were found to be almost circular and not agglomerated in nature [12].

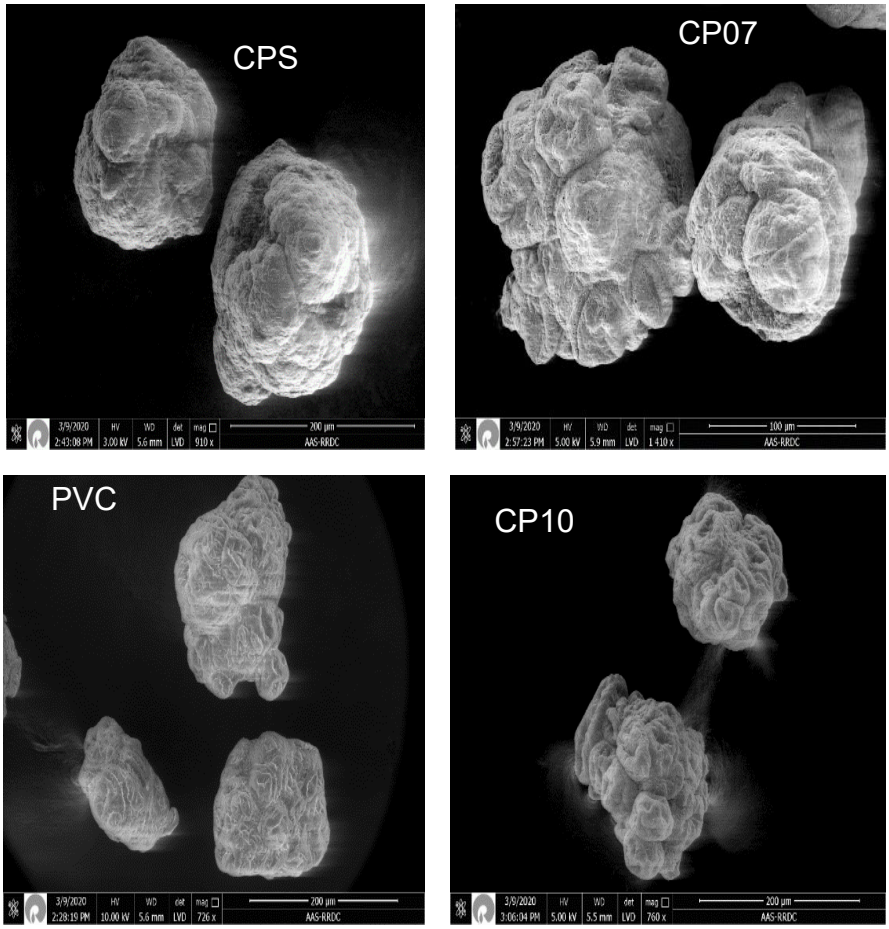


Figure 7. SEM morphology of PVC and chlorinated PVC resin.

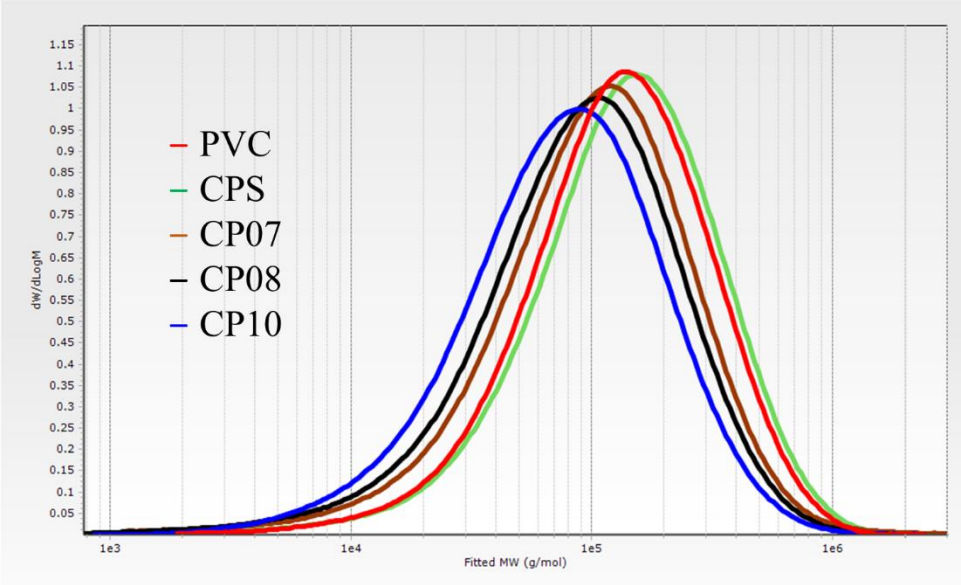


Figure 8. GPC analysis of PVC and CPVC resin.

Figure 8 showed the gel permeation chromatography (GPC) of synthesized CPVC. GPC analysis of synthesized CPVC samples showed slightly lower molecular weight as compared to the standard CPVC (CPS) and PVC resin due to thermal treatment of PVC macromonomer in presence of air which resulted in chain scission showed reduced molecular weight.

CONCLUSIONS

Thermally treated PVC resin in a static vacuum oven at 190°C for 30 minutes has resulted in the desired polyene concentration in the PVC chain. Unsaturation present in PVC chain after thermal treatment has been used for chlorination of PVC and synthesized CPVC. 13C NMR study confirms the enhancement of chlorine content in the PVC chain after the chlorination of PVC. The hydrogen peroxide (H_2O_2) initiator showed better performance as compared to benzoyl peroxide as H_2O_2 is miscible in DM water which is used as a solvent for CPVC reaction. The thermal analysis showed improvement in thermal stability after the chlorination of CPVC resin. The morphology of lab-synthesized CPVC resin was found like standard CPVC resin. The physical properties of chlorinated PVC resins were found comparable to the commercial CPVC resin. The process of synthesizing chlorinated PVC is a unique as waste and unsaturated PVC resin can be used to synthesize chlorinated PVC resin with better properties.

Acknowledgment

The authors would like to acknowledge Reliance Industries Limited (RIL) for providing the facilities and resources for the research work.

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