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Research Paper

Effect of Dechlorination and Ultrasonic Degradation on Suspension and Emulsion Grade of Poly (Vinyl Chloride).

Engineering

KEYWORDS : Polyvinyl chloride, Dechlorination, NaOH/EG solution, Polyvinyl alcohol.

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ABSTRACT

This study examined the dechlorination of different grades of polyvinyl chloride (PVC) under alkaline solution. Dechlorination under atmospheric pressure was carried out in NaOH/EG solution at 170^0 C - 200^0 C for 3 hours. This dechlorinated PVC was then subjected to ultrasonic degradation. Measurements of infrared (IR) spectroscopy, SEM, GPC and DSC were used to indicate the changes in PVC structure and properties due to formation of polyvinyl alcohol (PVAc) sequences in the polymer chain.

1. Introduction.

Recently recycling of waste plastics has received much attention not only by the government also by the people all over the world because of serious environmental problems caused by waste plastics, as well as their potential for use as resources. Waste plastics were treated by reclamation, incineration and recycling. Poly(vinyl chloride) (PVC), a widely used plastic knowing to its excellent properties, has caused problems in urban waste incineration.The reclamation treatment of Polyvinyl chloride (PVC) is inexpensive, but has many problems with instability of reclaimed sites due to the small specific density of plastics, which reduce the lifetime of product [1-2]. An important problem of incineration of poly (vinyl chloride) (PVC) is that its elimination of hydrogen chloride thereby accelerating corrosion of recycling plant components and produces a product stream containing environmentally toxic, chlorinated organic compounds [3]. Chemical recycling is an alternative method for minimizing the recurrent environmental problems of PVC residues. Despite the reactivity difference between PVC and its analogous low-molecular-weight compounds, PVC can be chemically modified by nucleophilic substitution of chlorine atoms in its structure. It was also reported that the thermal degradation of a PVC cause generation of poisonous product such as dioxins (2, 3, 7, 8-tetrachlorodibenzodioxin) [4] but few studies were found on the decomposition of commercial PVC materials from the standpoint of chemical recycling. PVC powder has been oxidized by oxygen in concentrated alkaline solution, and yielded benzene carboxylic acids and 34% of oxalic acid [5]. Dehydrochlorination of PVC in an alkaline solution is one method for the dechlorination, which had been studied by many researchers. A. Holländer et al., [6] poly (vinyl chloride) (PVC) with LiCl in dimethylformamide (DMF). Shin et al., [7] carried out the hydrolysis of rigid and flexible PVC in aq. NaOH at 150-250^{0}C for 0-12 h. Guo et al., [8] stated that the efficiency of dehydrochlorination increase by using Poly (ethylene glycol) as a catalyst with potassium hydroxide. Zhou et al., [9] established a new research of catalytical dechlorination of PVC using Al-Mg catalyst at 120^{0}c for 60 min. Sorensen et al., [10] described a combined wet oxidation and alkaline hydrolysis of PVC at 180^0-260^0 C for 8-24 min. However, their main interest in PVC hydrolysis is not in the dechlorination of PVC as a pretreatment for incineration. An advanced process was explained by Inoue et al., [11] which describes the Dechlorination of polyvinyl chloride by its grinding with KOH and NaOH in a planetary ball mill (7 steel balls) rotated at 600 r.p.m and volume treated was about 50 cm^3. It was concluded that NaOH reacts mechanochemically with PVC more mildly than KOH. Few mechanical degradation processes were studied by researchers, for example Okkuama [12] et al., proposed intensive ultrasonic degradation of polymer solution by cavitation mechanism. Basedow [13], Weissler [14], Langton and Vaughan [15], Melville and Murray [16], and Jellinek et al., [17] considered that the cavitation phenomena arising in an Ultrasonic field were responsible for the destructive processes. S. Chattopadhyay et al, [18] carried out the ultrasonic degradation of PVC solution (2 g L-1) under a sonic horn (20 kHz and 180 W).

The present study is a combination of dechlorination treatment and ultrasonic degradation process of PVC and its different grades (emulsion and suspension). This includes a comparative study of the effect of dechlorination and ultrasonic degradation on various grades of PVC.

2. Experimental

2.1. Materials

PVC suspension grade [MW = 83735] and PVC emulsion [MW = 84805] containing approx. (53% of Cl) was produced of reliance industries and chemplast (India) respectively. Material had been well dried and stored at 60^{0}C before use. Standardized 0.010 Mol/L $AgNO_3$ was used to determine the chlorine concentration. All other reagents were purchased from SD Fine Chemicals India.

2.2 Dechlorination of PVC in NaOH/EG solution.

The dechlorination reaction was carried out, 500-mL, Pyrex flask with 10 g of PVC powder in 250mL of 2M of NaOH/EG. The flask was heated to between 150^{0}C and 210^{0}C, with a step change 15 min for each 10^{0}C to reach the final temperature. The reaction mixture was held between 150^0-190^{0}C with mild agitation provided by a stream of N_2 to create inert environment. Immediately after completion of reaction the product were filtered through a glass-fibre filter, and then washed repeatedly with deionised water and methanol. The chlorine content of the product was measured by potentiometric titration method. Residual C, H, and Cl were determined by elemental analyses. The residue was also measured by diffuse reflectance Fourier transform-infrared spectroscopy (FT-IR).

2.3 Ultrasonic degradation of dechlorinated PVC.

20 mL of DPVC solutions in THF (2 g L^{-1}) was taken in a 50 cm^3 glass beaker and the beaker was kept in a constant temperature ultrasonic bath. Use of bath will also reduce the vaporization loss of solvent during ultrasonication. The ultrasonic waves were switched on after the solution attains the bath temperature with a start period for 60 sizes and stop period of 30sec.Samples were collected after 60 min of ultrasonication time for analysis by gel permeation chromatography (GPC).

2.4 Calculation of degree of dechlorination (DD).

Degree of dechlorination can be found by calculating the monomeric unit of material (n), dechlorinated product (m) and unreacted PVC (l) eq 1 [19]. Unit number "m" is calculated by the difference of n and l.

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$$DD\ (\%) = 100 \times \left(\frac{m}{n}\right)\ (\%) \qquad (n=m+1) \qquad \text{eq (1)}$$

As in partial dechlorination it very difficult to measure the chlorine drop from above equation.

To determine mass ratio, we assume that on polymeric chain few chlorine were replaced by hydroxyl group and thus chain obey the fox equation eq 2 [20,21] of mass fraction and glass transition temperature.

$$T_g = W_1 T_{g1} + W_2 T_{g2} \qquad \text{eq (2)}$$

Where and are weight fraction of different polymers in a mixture and for their respective glass transition temperature. The glass transition can be determined by differential scanning calorimetry analysis. This method gives us the percentage of polyvinyl alcohol formed by dechlorination which is equal to the amount of chlorine removed. The colour of the product when washed and dried became yellow. Dechlorination degree (DD) of PVC to PVA reached 46.42% and 58.2% for suspension and emulsion grade of PVC respectively.

2.5 Molecular weight analysis.

The sonicated samples were injected in the GPC (Agilent tech. $V_1$0306) for molecular weight analysis. Tetrahydrofuran was used as eloquent and it was pumped at a constant flow rate of 1.0 mL/min. The columns were maintained at 40^{0}C with a column heater. The refractive index was continuously monitored to obtain the chromatograph. The chromatograph was converted to molecular weight distribution by the use of a calibration curve. Calibration was based with polystyrene as the standard.

2.6 Analysis and sample preparation

2.6.1 Estimate chlorine in dechlorinated PVC by potentiometric titration.

Pre-weighed of PVC sample (4-5 g) was added to 2 g of Na_2CO_3 and heated in to muffle furnace at 500^{0}c for 3 hrs. The mixture was then cooled to room temperature and 10 mL of distilled water and methyl orange indicator was added to it. The obtained solution was neutralized with 30% HNO_3 and to this 30 mL of acetone was added to it. The solution was then titrated potentiometrically with N/100 $AgNO_3$ solution (T_s). A mixture (T_b) was again prepared without using PVC. The percentage chlorine content can be evaluated by the difference in EMF end point titration of sample (T_s) and blank (T_b) results as shown in eq 3.

$$\frac{T_s - T_b \times 35.5}{W} \qquad \text{eq (3)}$$

2.6.2 Determine the polyvinyl alcohol weight fraction after dechlorination.

This analysis was based on the fox equation as explained in earlier section, which require the determination of glass transition temperature by using differential scanning calorimetry (DSC). The Tg of pre-dried PVC, dechlorinated PVC and Polyvinyl alcohol were computed on DSCQ100 analyzer T.A. instrument with temperature range 0 - 250^{0}C in an inert atmosphere of nitrogen (50.0mL/min).

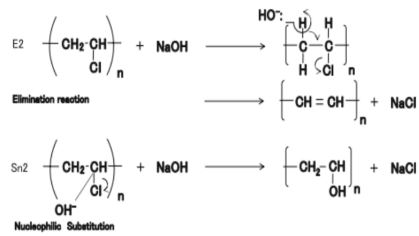
2.6.3 Characterization.

Structures of PVA samples obtained by the partial hydrolysis of PVC and pure PVC reagents were examined by reflectance Fourier transform infrared spectroscopy (FT-IR). Infrared spectra of the residue were obtained by FT-IR (Bruker), and the morphology of the residue was examined by scanning electron microscopy (SEM) (icon analytical lab).

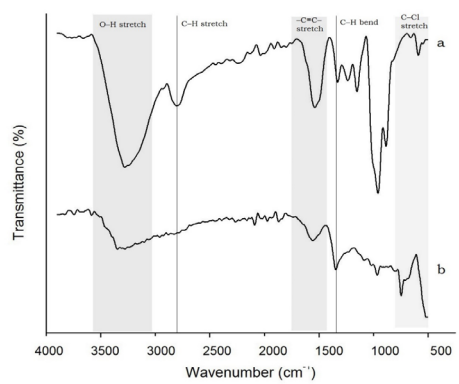
2.5 Results and discussion

Dechlorination of PVC in the NaOH/EG Solution.

After dechlorination the suspension grade and emulsion grade of PVC physical appearance changes from white to yellow in colour. The DPVC-Suspension obtained was pale yellow in colour, whereas the DPVC-Emulsion is dark yellow in colour. The increase of the length of the conjugated double bonds corresponds also with the change of the colour of the product from white to yellow, orange, red, brown, and black [22], as the product obtained was yellow in colour indicate that dechlorination was followed by SN_2 reaction as that of E2.No change in colour of DPVC was observed for both grades when they were subjected to ultrasonic degradation in solution state. As ultrasonic waves only reduce the chain length by cavitation mechanism, whereas chemical structure was preserved Fig. 1 shows FTIR spectra a) PVC demonstrates the absorption bands of C-Cl is stretching vibrations (around 650 cm^{-1}), b) residual particles obtained following dechlorination in 1.0 M NaOH/EG, c) DPVC-Suspension after 180 min and d) DPVC-Emulsion after180 min. The transmittance bands representing the stretching vibrations of O–H (the large absorption band centred at (3500 cm^{-1}),



Scheme 1 Elimination and Nucleophilic mechanisms of Substitution reaction of poly(vinyl chloride) in NaOH system.



–C–H (methane 2900 cm^{-1}), C=C (~1600 cm^{-1}) and stretching vibration of C–Cl (750 cm^{-1}. The intensity of stretching vibration of C-Cl is higher in the DPVC-Suspension as compared to the DPVC-Emulsion, which indicate more chlorine atoms get substituted by hydroxyl molecule in emulsion grade that that of suspension grade. The FTIR spectra also confirm the substitution of Cl by OH through S_N2 mechanism.

Fig.2 shows the degree of chlorine present in the PVC before and after the dechlorination, dechlorination was defined as the mole percent Cl react with the $AgNO_3$ during potentiometric titration.

Ag^+ (aq) +Cl^- →AgCl(s)

When the chlorine reacts with the silver ions from $AgNO_3$ an immediate increase in the electromotive force can be seen, this occurs due formation of AgCl in the reaction as a precipitation. Which shifts the graph to the upper stage and the corresponding value of volume will be the end point. To observe the sharp end point Fig 3 was compiled, which shows the peak at end point when plotted with change in EMF w.r.t to change in volume Vs volume. Fig. 2 shows that the volume of AgNO3 required (end point) to react with chlorine is higher for virgin PVC sample and after dechlorination the significant drop in the end point was observed.

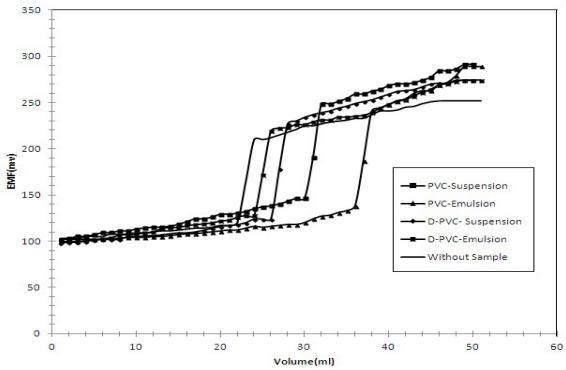


Figure 2 Potentiometric titration graph (emf vs volume) of normal and dechlorinated poly (vinyl chloride) for determination of chlorine content.

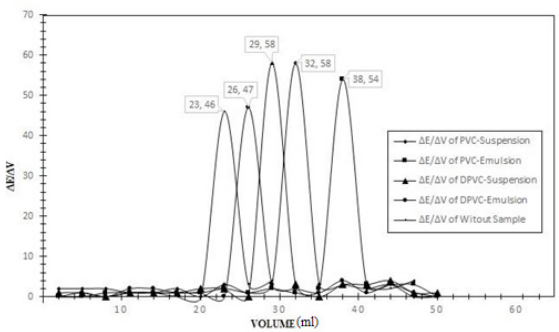


Figure 3 Potentiometric titration graph (Change in emf vs volume) of normal and dechlorinated poly (vinyl chloride) for determination of chlorine content.

From equation 3(Potentiometric analysis equation), it was obtained that the PVC-Suspension and PVC-Emulsion has the chlorine approx. 53.25% and 47.33%, respectively. But after dechlorination the chlorine content drops to 29.58% and 23.33 % for D-PVC-Suspension and D-PVC-Emulsion respectively. The dechlorination is higher in the emulsion grade PVC, because of two reasons a) PVC-Emulsion is having a high surface area and small particle size (4.06μm) due to which the rate of dechlorination is high as compared to suspension grade b) Emulsion grade material get easily dispersed in NaOH/EG solution than that of suspension based PVC.The dechlorination of PVC in NaOH/EG was expressed as an apparent first-order reaction. The degree of dechlorination increased with reaction time and increasing NaOH concentration.

SEM analysis shows that the emulsion grade (DPVC-Emulsion) is more significant undergoes the dechlorination reaction when compared with the suspension grade (DPVC-Suspension). The Fig.4, Shows images of (a) unreacted PVC-Emulsion powder and the residues (b) unreacted PVC-Suspension grade (c) reacted DPVC-Emulsion and (d) reacted DPVC-Suspension obtained by dechlorination in the NaOH / EG system. The emulsion grade (PVC-Emulsion) has the spherical shaped particle as that of pearl. After dechlorination the spherical shape of the particle gets fractured, particle get swell and break into small fragments. During the reaction, this fracturing would result in an increased surface area of PVC powder, thereby enhancing contact between the PVC powder and dissolved OH^-. Similarly, in the case of suspension grade (PVC-Suspension) a bead like shape of particle was observed. When it was subjected to the dechlorination this bead get fractured into rod like particle.

In emulsion grade Fig (c) it can be seen that small spheres are coming out of the larger one and dispersed into the system after dechlorination and degradation. Whereas in suspension grade Fig (d) a rod like structure can be seen. Due to a higher degree of hydrolysis in emulsion the resulting particle have shaped as a sphere and lower degree of hydrolysis leads to formation of rod like shape in suspension grade after dechlorination and degradation. This ultimately results in the higher dechlorination and degradation efficiency observed in emulsion grade versus suspension grade.

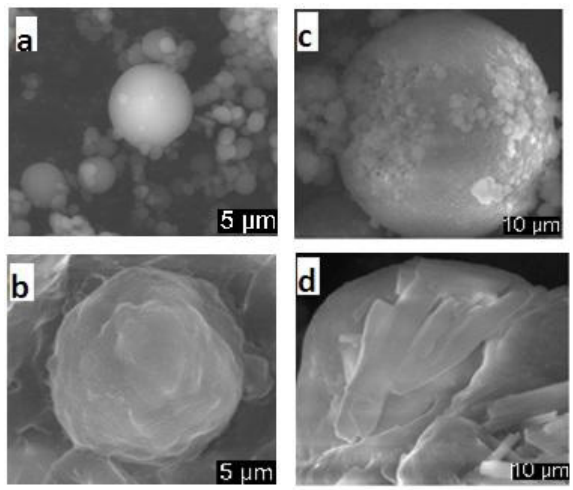


Figure 4 Comparative SEM images of a) Normal PVC-emulsion grade b) Normal PVC-suspension grade c) Dechlorinated PVC-emulsion grade and d) Dechlorinated PVC-suspension grade

2.6.2 Weight fraction of Substituted chains.

The partial dechlorination leads to formation of polymeric chain which consist of Poly (vinyl chloride) and substitution of the hydroxyl group in a same chain. As a result the glass transition temperature of the dechlorinated product is being experimentally observe in the range of glass transition temperature of Poly (vinyl chloride) and Poly (vinyl alcohol). Fig 5 shows the DSC graph non treated emulsion and suspension grade of poly (vinyl chloride) (Fig.5a and 5b) and poly (vinyl alcohol) (Fig 5c). As there is a slight difference in glass transition temperature of suspension and emulsion grade, because of the presence of surfactant traces the emulsion grade of poly (vinyl chloride). Fig 4 shows the DSC graph of emulsion and suspension grade of dechlorinated PVC (Fig.5d and Fig.5e). As due to replacement of few chlorine molecules with hydroxyl group from the main chain of PVC in dechlorination, a blended chain was obtained which results in the drop of glass transition temperature in both grades. In DPVC-Emulsion the glass transition temperature is nearer to the glass transition temperature of PVAc which shows that the large fraction of PVC got substituted. Whereas the glass transition temperature of DPVC-Suspension is in mid of glass transition temperature of PVC and PVAc. As only a few molecules undergone dechlorination process.

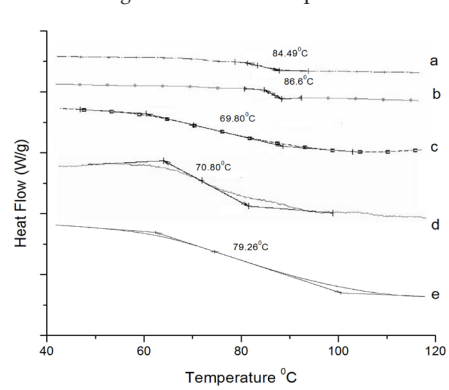


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Figure 5 DSC thermograph comparing the change in glass transition temperature a)suspension PVC, b)emulsion PVC, c)poly(vinyl alcohol) and d)dechlorinated PVC

From the table MWDs of the sonicated samples which were determined by GPC, it was observed that only a small drop in the molecular weight was achieved after dechlorination. As due to cavitation phenomenon the drop after ultrasonication become more significant, but higher drop was observed when the dechlorinated PVC was subjected to the sonication in solvent.

Grade	M_n	M_n after dechlorination	M_n after ultrasonic degradation
Suspension PVC	83735	78541	68511
Emulsion PVC	84805	74310	69542

Table 1 Molecular weight analysis (GPC) explaining effects of dechlorination and ultrasonic degradation

In both DPVC-Suspension and DPVC-Emulsion the drop in molecular weight is nearly same. Whereas the degree of dechlorination in DPVC-Emulsion is higher than that of suspension. It means that the dechlorination reaction contributes a share than that of ultra-sonication in reducing the molecular weight of the polymer. But dechlorination eliminate the formation of Hall during degradation and offer a controlled rate for PVC degradation.

Among several solvents available, THF and water were finally chosen as a solvent for PVC and DPVC for dissolution test. Because of the substitution of hydroxyl groups in the main chain of polyvinyl chloride in dechlorination and chain separation by ultrasonic degradation, it was seen that the polymer is neither completely soluble in THF nor in the water. But when partially soluble DPVC in THF was mixed with the partially soluble DPVC in water a homogenous solution is observed. Whereas when DPVC in THF was mixed with water (containing no polymer) a precipitation in solution was observed. Fig. 6 shows the nature of solutions a) THF and Water, b) PVC-S in THF but not in the Water) PVC-E in THF but not in water, d) DPVC-S in THF but not in water, e) DPVC-S (THF) and DPVC-S (water), f) DPVC-E (THF) and water and g) DPVC-E (THF) and DPVC-E (water). From the test it is clear that we obtain a homogeneous solution of mixture either when polymer is present in both solvent or absent in both. When both THF and water (containing no polymer) was mixed with a clear solution was observed Fig. 6(a). Whereas in Fig. 6(b) the PVC-Suspension is only present in THF, so when water (containing no polymer) was added a white precipitation was observed. Similarly, it is for the PVC-Emulsion Fig. 6(c). In Fig. 6(d, f) DPVC-Suspension and DPVC-Emulsion respectively in THF gives a yellow colored precipitate when mixed with water, the coloration in precipitate is due to dechlorination and degradation. But when DPVC-Suspension in THF was added to DPVC-Suspension Fig. 6 (e) in water with the same volume, a homogenous solution was observed. The same nature was followed by DPVC-Emulsion in THF and DPVC-Emulsion in water Fig. 6 (g). The emulsion grade imparts darker color in homogenous solution than that of suspension grade. It is due to more degradation in emulsion grade as compared to suspension grade. It also supports the fact that substitution of hydroxyl groups in PVC is higher in the emulsion grade than that in suspension grade.

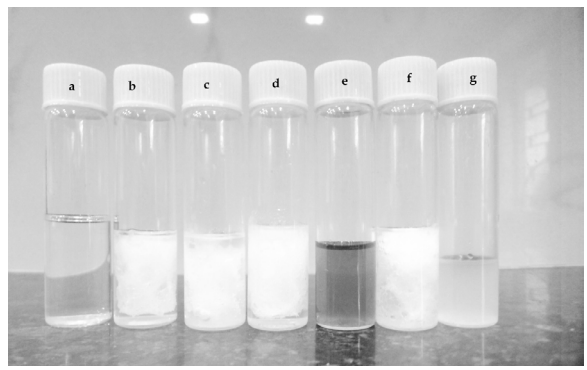

Figure 6 Dissolution and precipitation test comparison a) THF and Water, b) PVC-S in THF but not in the Water) PVC-E in THF but not in water, d) DPVC-S in THF but not in water, e) DPVC-S (THF) and DPVC-S (water), f) DPVC-E (THF) and water and g) DPVC-E (THF)

3. Conclusion.

Suspension and emulsion grade of PVC was dechlorinated in NaOH/EG and degraded by ultrasonic energy. The chlorine content of PVC-Emulsion and PVC-Suspension after dechlorination was found to be 23.33% and 29.58% respectively. Emulsion grade PVC is more susceptible for dechlorination because of the higher surface area present to reaction and ability to got dispersed in NaOH/EG solution. The process yield to a heterogeneous product that showed different proportions of elimination products, hydroxyl substitution and no harmful products such as hydrochloric acid and dioxins were produced. Dissolution test show that the product from a stabilize solution without any precipitation when both THF and water were mixed

REFERENCE

1. Bevis M. Secondary recycling of plastics Materials in engineering 1982 (3) ; 344-349 2.Brandrup J, Bittner M, Menges G, Michaeli W. Recycling and recovery of plastics, Hanser Publishers, New York 1996 ; 240-261. 3.Troitskil B , Troitskaya L, Myakov V & Lepaev A. Mechanism of the thermal degradation of poly(vinyl chloride) J.Polymer Science 1973 (42) ; 1347-1361. 4.Theisen J, Funcke W, Balfanz E, Ko¨nig. Determination of PCDFs and PCDDs in fire accidents and laboratory combustion tests involving PVC-containing materials J. Chemosphere 1984 (19) ; 423-28 5.Yoshioka, T., Yasuda, S., Kawamura, K., Sato, T. and Okuwaki, A., Nippon Kagaku Kaishi, 534(1992). 6 .Holländer A, Zimmermann H, Behnisch J. Chemical dehydrochlorination of poly (vinyl chloride) by LiCl in dimethylformamide Polymer 1992 (33) ; 637–642. 7.(a) Shin S, Yoshioka T, Okuwaki A. Dehydrochlorination behavior of rigid PVC pellet in NaOH solutions at elevated temperature Polym Degrad Stab 1997 (61); 349-53. (b) Shin S, Yoshioka T, Okuwaki A. Dehydrochlorination behavior of flexible PVC pellets in NaOH Solutions at Elevated Temperature J Appl Polym Sci 1998 (67) ; 2171-7. 8. Guo L, Shi G, Liang Y. Poly(ethylene glycol)s catalyzed homogeneous dehydrochlorination of poly(vinyl chloride) with potassium hydroxide J.Polymer 2001 (42) ; 5581-5587. 9. Zhou Q, Tang C, Wang Y, Zheng L .Catalytic degradation and dechlorination of PVC-containing mixed plastics via Al–Mg composite oxide catalysts Fuel 2004 (83); 1727–1732 10.Sorensen E, Bjerre B. Combined wet oxidation and alkaline hydrolysis of polyvinylchloride Waste management 1992 (12) ; 349-354. 11 Inoue T, Miyazaki M, Kamitani M, Kano.J, Saito F Dechlorination of polyvinyl chloride by its grinding with KOH and NaOH Advanced Powder Technol.2005 (16) ; 27-34. 12.Okkuama M, Hirose T. Mechanics of ultrasonic degradation of linear high polymer and ultrasonic cavitation J. App.Polymer 1963 (7) ; 591-602. 13. Basedow A, Ebert K. Ultrasonic degradation of polymers in solution Adv. Polymer Sci. 1977(22); 83-148. 14. Weissler A. Cavitation in Ultrasonic Depolymerization J. Acoust. Soc. Amer. 1951 (23); 370. 15. Langton N, Vaughan P. Cavitation and the ultrasonic degradation of high polymers 1 Br. J. Appl. Phys. 1962(13) ; 478-481 16. Melville W , Murray J.R, Degradation of polymers the ultrasonic degradation of polymers Trans. Faraday Soc.1950 (46) ; 996. 17 Brett H, Jellinek H, Degradation of long chain molecules by ultrasonic waves. Part V. Cavitation and the effect of dissolved gases J. Polymer Sci. 1954 (13) ; 441–459 18. S.Chattopadhyay & G.Madras, Influence of temperature on the ultrasonic degradation of poly(vinyl acetate) and poly(vinyl chloride) Journal of Applied Polymer Science, Vol. 88, 2818 –2822 (2003) 19. Yoshinaga T, Yamaye.M, Kito T, Ichiki T, Ogata M, Chen J, Fujino H, Tanimura T, Yamanobe T. Alkaline dechlorination of poly(vinyl chloride) in organic solvents under mild conditions Polym Degrad Stab 2004(86);541-547. 20.Hiemenz, Paul; Timothy Lodge (2007). Polymer Chemistry. Boca Raton, Florida: CRC Press. 21.Fried.J Polymer Science And Technology,Second edition.PHI learning Pvt.Ltd (India)2010,ISBN-978-81-203-2770-2,181. 22.Yoshioka T, Kameda T, Imai S, Noritsune M, Okuwaki A. Dechlorination of poly(vinylidene chloride) in NaOH/ethylene glycol as a function of NaOH concentration, temperature, and solvent Polym Degrad Stab 2008(93); 1138–41.