Management of waste poly vinyl chloride (PVC) through chemical modification

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This review presents a strategy for management of poly vinyl chloride (PVC) waste by chemical modification as a viable method. PVC contains chlorine as a source to attack by nucleophiles (Nu⁻) and resultant product can be used for various applications due to its conductivity, antibacterial and ion exchange properties. Prominently used Nu⁻ are I⁻, SCN⁻, OH⁻, N₃⁻, phthalimide anion and concentrated alkali solution in the presence of O_2 as oxidants.

Keywords: Antimicrobial, Chemical modification, Nucleophilic substitution, Polyvinyl chloride (PVC), Waste management

Introduction

Due to specific fire retardant nature, polyvinyl chloride (PVC) polymers have widest ranges of applications in plastic industry, particularly in electronics products. At global level, demand for PVC exceeds 35 million t/y, and it is rated second only after polyolefins as volume leader in plastics industry[1-7]. Management methods include landfilling, incineration, mechanical recycling and chemical modification. Due to space constrain and associated soil infertility, landfilling is not a suitable method for management of resultant waste[1,3,8]. Waste PVC products can be recycled by pyrolysis in incinerator[5]. Different thermal and catalytic degradation methods include the use of slow pyrolysis in a bubbling fluidized bed[9] and steam gasification process[10]. Emission of large amount of corrosive hydrogen chloride gas and other harmful products like dioxin, furan are disfavors incineration as a possible management technique[3,11,12]. Mechanical recycling techniques include remelting and shaping, resulting a poor quality products[2,4,13]. Chemical modification of waste PVC is new and emerging area for the management of resultant waste[8,14-21]. This review proposes management techniques of waste PVC through chemical modification as a viable method and its possible research aspects.

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Dechlorination and Recycling of PVC Waste

PVC is dechlorinated for its feedstock recycling and chlorine thus released as hydrochloric acid (HCl) depends upon particle size, chemical agent, temperature and catalyst[3-5,15,22,23]. Dechlorination of PVC wastes is usually done by thermal cracking via hydrogenation, pyrolysis or gasification[12,21,24-28] and degradation products are HCl, gaseous and liquid hydrocarbons, and char in inert atmosphere. Thus obtained HCl can be reused either in vinyl chloride production, or in other chemical processes[24]. In a steam atmosphere at high temperatures, hydrocarbon fraction can be converted into carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2)[4,5,13].

Mechanochemical (MC) methods are alternative way for dechlorinating PVC by grinding using a planetary ball mill[29-31] with dechlorinating reagent like CaO, without any heating operation. MC method has a high potential to dispose of PVC wastes at any desired location with flexible operation due to its use of a portable facility composed of a mill and a washing tank with a filter. Other used additive is a mixture of $CaCO_3$, SiO_2, and Al_2O_3[32]. MC dechlorination proceeds as grinding progresses and improves with an increase in both the mill speed and the amount of balls introduced into the mill[24]. First step in PVC degradation is the evaluation of HCl, then color develops, and polymer eventually becomes stiff and insoluble as a result of crosslinking. Free radicals may

also result from the ejection of a chlorine atom from a polymer chain. At room temperature (RT), chlorine atoms may be formed as a result of the absorption of light energy[33]. Once radicals are produced, degradation in the presence of oxygen may take many routes. Some researchers proposed MC decomposition of PVC by using La_2O_3 as additive[34].

In a bench-scale bubbling fluidized bed, main intermediate product after dechlorination is a polyene material that continues to degrade by the evolution of aromatics and converted into products. Their composition will be strongly determined by processing variables (atmosphere, temperature and residence time)[4]. Use of catalytic inactive solid quartz as bed material results in the production of large amounts of char and tar, whereas application of catalytic active porous alumina results in a high conversion of PVC into syngas. Moreover, temperature has a large impact on the composition of products, as carbon to gas conversion was 70% at 1150 K, and improved to 100% at 1250 K.

Successful recycling attributes to the extent of dechlorination[35]. Hence attempts have been made to increase dechlorination via variation of operating parameters or using new chemicals within the feed. Masuda *et al*[36] studied dechlorination and associated thermal decomposition of mixture of PVC and various metal oxides, and demonstrated that emission of HCl changes significantly with the oxides used, indicating chlorine fixing ability of oxides. However, chlorine content could also be recovered as HCl by adjusting alkali concentration[5,11]. Mild alkaline hydrolysis of PVC in an organic solvent was conducted with a satisfactory degree of dechlorination and resulting hydrolysis product is poly (vinyl alcohol) with very small chlorine content. Sodium chloride was the only by-product[37].

Management of PVC by Chemical Modification

PVC containing chlorine is used as a source to be attacked by nucleophiles (Nu) and resultant product possesses distinguished properties inherited from its parent product. This modified product can be used for various applications due to its conductivity, and antibacterial and ion exchange properties. This strategy can provide an emerging opportunity for the management of PVC waste.
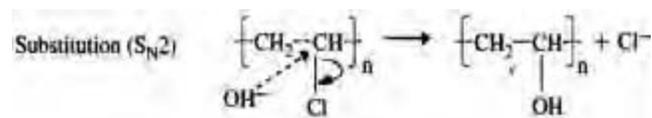
Chemical Modification by Oxidation

Oxidative degradation processes of PVC are proposed as viable technique for recycling of PVC waste

materials[38]. In UV initiative degradation, formed peroxides are thermolysed to give carbonyl compounds[39,40]. PVC powder is oxidized by oxygen in an alkaline solution (conc.), yields benzene carboxylic acids and oxalic acid[41,42]. Mechanism like radical-chain transfer reaction of zipper-type may well account for this type[43]. Water-soluble acids are obtained by oxidation of PVC in alkaline oxygen solutions[44]. Alkali concentration plays important role towards dehydrochlorination and maximum rate is reached at 5M NaOH for flexible PVC[45]. Yoshioka *et al*[11] obtained 320 g of oxalic acid and 130 g of benzenecarboxylic acids (as phthalic acid) from 1 kg of F-PVC under conditions of a 15-M NaOH solution at 250°C and a P_{O2} of 5 MPa for 5 h. Sorensen & Bjerre[44] described a combined wet oxidation alkaline degradation of PVC powder; reaction is highly accelerated under oxygen supply and products are mainly HCl and CO_2, besides a wide range of water-soluble organic compounds including benzaldehyde.

Chemical Modification by Nucleophilic Substitution

Labile chlorine atoms of tertiary and allylic chlorines and normal secondary ones coupled with a varying content of carbon–carbon double bonds present in PVC are responsible for numerous chemical modifications[46]. This subject has been broadened by widespread ongoing research using nucleophiles[33-36,47]. Reaction extent is observed to be higher as solvent polarity increases and stereoselective character of reaction holds only for solvents containing C=O[48]. This dechlorination substitution reaction in presence of alkali solution occurs by a combination of SN2 mechanisms[49] as

Some researchers propose chemical modification by $Ca(OH)_2$ instead of NaOH but at slower reaction rate due to low solubility of $Ca(OH)_2$[50]. Chemical modification of PVC in nucleophile (Nu)/ethylene glycol (EG) or Nu/ N,N-dimethylformamide (DMF) solution result in substitution of Cl in PVC with Nu from solution. For SCN^-, OH^-, and N_3^-, degrees of substitutions were relatively high (20%). For I^- and phthalimide anion, it was 1.6 and 6.0% respectively[51]. When PVC was treated in Nu/DMF solution, with a Nu/Cl (in PVC) molar ratio of 4, even though reaction conditions were different, degree of substitution was high, in the order $N_3^- > SCN^-$

> phthalimide anion > I⁻. Highest degree of substitution was for N_3^- (66.1%). In both EG and DMF solutions, order of the ratio of substitution to dechlorination was similar to that of nucleophilic reactivity constant, I⁻ > SCN⁻ > N_3^- > phthalimide anion, except for I⁻. Low ratio for I⁻ is attributable to elimination of HI after substitution of Cl in PVC, with I⁻ in solution, because I⁻ is strong Nu and an excellent elimination group. Comparing effect of EG and DMF on substitution of Cl in PVC with Nu in solution, substitution to dechlorination ratio was higher for I⁻, SCN⁻, N_3^-, and phthalimide anion in DMF than in EG. Substitution of Cl in PVC with Nu in solution was found to occur preferentially in DMF versus EG.

Substitution/dehydrochlorination ratio depends on solvent polarity and decrease in the order of EG > di-EG > tri-EG[52]. Also, reactions of rigid PVC with various Nu (iodide, hydroxide, azide, and thiocyanate) in EG as solvent are reported[16]. Such reactions lead to substitution of Cl by Nu and finally elimination of HCl, resulting in dehydrochlorination of rigid PVC. Dehydrochlorination yield increased with an increasing Nu concentration, resulting in a maximum substitution at high Nu amounts. Moreover, when EG was replaced by di-EG, dehydrochlorination accelerated, may be due to higher compatibility of di-EG with PVC, making it easier to penetrate rigid PVC particles. Machado *et al*[53] have described a process, in which PVC have chemically modified to produce a sulfonated polymer with dehydrochlorinated while chemical modification of PVC with bifunctional thiol compounds[54-56] and sodium sulfide[57] is also reported in some another study.

Polyethylene glycol (PEG)s [HO(CH₂CH₂O)ₙH, where *n*> 3] are highly active and selective in catalyzing dehydrochlorination of PVC in organic–aqueous hydroxide two-phase systems[58]. An improvement of dechlorination was actually observed for di-EG and tri-EG compared with EG[59]. Utilization of PEG can accelerate dehydrochlorination of PVC[35], so that at 210°C for 1 h dehydrochlorination degree was as high as 74% for PVC/PEG, while for PVC, it was only 50%. Moreover, for PVC/ PEG, decomposition of PVC shifted to lower temperatures compared with that of pure PVC, suggesting some interactions exist between PEG and PVC that caused faster dehydrochlorination rate. Guo *et al*[60] performed extensive dechlorination of PVC using a homogeneous solution of potassium hydroxide (KOH) in THF and PEG at RT.

Chemical modification of PVC is reported by amination using concentrated aqueous solution of ethylenediamine. Aminated PVC is reacted with hexamethylene diisocyanate to incorporate isocyanate group onto polymer backbone and resultant PVC is further reacted with PEG (mol wt, 600 Da)[61]. Bulk modification of PVC with PEG using appropriate chemistry can give rise to a polymer that possesses anti-fouling property of PEG and such bulk modifications are less cumbersome compared to surface modifications on finished product to impart anti-fouling properties to PVC surface. Aqueous ammonia was found to be most suitable in hydrothermal dechlorination of PVC. Dechlorination with aqueous ammonia proceeded in three stages (initial incubation, major dechlorination, and slow dechlorination). In initial stage, rates were very slow and scarcely affected by temperature or ammonia concentration. In second stage, extensive dechlorination took place, and rates were affected by temperature and ammonia concentration[62].

PEG accelerates dehydrochlorination of PVC. For PVC/PEG, decomposition of PVC corresponding to dehydrochlorination stage shifted to lower temperatures compared with that of pure PVC, suggesting some interactions between PEG and PVC that caused faster dehydrochlorination rate. In addition, during this process, no waste byproducts (KCl) have been produced, and satisfactory recyclability of PEG (10 cycles) has been obtained[12]. Phase-transfer catalysts tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogen sulfate (TBAHS) significantly influenced chemical modification of PVC by substitution with thiocyanate as a Nu[63]. TBAB accelerated dechlorination of PVC in SCN/ EG solution. Addition of TBAB to SCN/EG solution improved substitution of Cl in PVC with SCN in solution. Addition of TBAB or TBAHS to SCN/H₂O solution promoted dechlorination of PVC, whereas dechlorination did not occur without catalyst[64].

Application of Chemical Modification on PVC

PVC by wet-chemical modification can be used in antimicrobial activity[65] and Gram-negative bacteria of strains *Staphylococcus capitis*[66]; *S. aureus* and *S. epidermidis*[67] are reported using thiocyanate modified PVC. Some researchers proposed use of ferrocene modified PVC in electron transducer in electrochemical ion sensors[68]. Looking into possible chemical modification in PVC and properties of resultant products (Table 1), it has been observed that: i) in EG medium and 190°C using Nu⁻ like SCN⁻, N_3^-, OH⁻, 95% dechlorination was achieved and resultant products had antibacterial and conductive

Table 1—Chemical modification in PVC and properties of resultant product

Degree of dechlorination/ Chemical modification	Nucleophile (Nu)/ Condition	Properties of resultant product
98% Dechlorination[52]	SCN⁻ / EG at 190°C; 6 h	Antibacterial activity
> 95% Dechlorination[52]	N₃⁻ / EG at 190°C; 1 h	As functional polymers
60% Dechlorination[52]	I⁻ / EG at 190°C; 8 h	As ion-exchange resin
>95.0% Dechlorination[52]	OH⁻ / EG at 190°C; 1 h	Conductive properties
100.0% Dechlorination[45]	3 M NaOH at 250°C; 5 h	Porous char
Oxidation[45]	15 M NaOH and P_{O2} = 5MPa; 250°C; 5 h	32% Oxalic acid; 13% Benzene carboxylic acid
1.8% Substitution[16]	SCN⁻ with THF- DMSO in 1: 1	Antibacterial activity
3.8% Substitution[16]	SCN⁻ with THF- DMSO in 1: 2	Antibacterial activity
2.0% Substitution[16]	SCN⁻ with THF- DMSO in 1: 4	Antibacterial activity
98.5% Dechlorination[16]	SCN⁻ / EG at 190°C; 8 h	Antibacterial activity
97.3% Dechlorination[16]	SCN⁻ / EG at 170°C; 24 h	Antibacterial activity
10.9% Dechlorination[16]	SCN⁻ / EG at 150°C; 48 h	Antibacterial activity
18.7% Substitution[52]	SCN⁻/DMF at 100°C; 24 h	Pale pink product
66.1% Substitution[52]	N₃⁻ / DMF at 100°C; 24 h	Black product
10.5% Substitution[52]	Phthalimide / DMF at 60°C; 12 h	Black product
3.6% Substitution[52]	I⁻ / DMF at 60°C; 24 h	Pale yellow product
97.8% Dechlorination[37]	1M NaOH /EG at 190; 45 min	Porous char

properties; ii) 100% dechlorination was achieved in 5M NaOH at 250°C and resultant product can be used as porous char; and iii) under the condition 15M NaOH, 5 MPa P_{O2} and 250°C, obtained product was 32% oxalic acid and 13% benzene carboxylic acid.

About half of PVC is in use in long-life products (building, packaging, furniture, electric/electronics, automotive etc.) and lifespan of such PVC products is 30-40 y, so a significant increase in PVC waste generation is expected in the near future. In an estimation, PVC waste at European Union in 2010 was 5.4 million tons (MT), which is projected to reach 7.1 MT in 2020[69,70]. Here, chemical modification will be a valuable alternative method for management of waste PVC.

Conclusions

Management of PVC related municipal solid wastes by landfilling or incineration has limitation due to resultant environmental pollutions. This review addressed issues related to existing management and suggests the role of chemical modification as a valuable alternative method for management of waste PVC. In the case of UV imitative degradation, initially formed peroxides are thermolysed to give carbonyl compounds. Water-soluble acids are obtained by oxygen oxidation of PVC in alkaline solutions. Dehydrochlorination of PVC in flexible PVC proceeds by a first-order reaction in alkaline solution. Maximum rate of dehydrochlorination for flexible PVC is reached at 5M NaOH. In the course of PVC oxidation,

NaOH follow a radical-chain transfer reaction of zipper-type.

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