EVALUATION OF THE DEHYDROCHLORINATION OF POLYVINYL CHLORIDE IN STEAM ATMOSPHERE

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Abstract

The current research evaluates a process using steam for the acceleration of the thermal dehydrochlorination of polyvinyl chloride (PVC) resin and flexible PVC. This process is aiming on waste streams such as medical equipment containing PVC, which also requires a mandatory sterilization treatment. Thus, steam could act simultaneously as dechlorination and sterilization agent.

Keywords: *Dehydrochlorination; Atmospheric pressure; Medical waste*

1. Introduction

Polyvinyl chloride (PVC) is a versatile material. However the disposal of PVC-based waste is problematic because of its high content of chlorine. When incinerated, it is prone to produce HCl which corrodes equipment, and is also a precursor for dioxin formation. This results in the release of hazrdous pollutants into the atmosphere. Among the many applications of PVC, medical tubing made from flexible PVC is of interest for this research. A process using steam that could be implemented to fulfill both the need of sterilization and dehydrochlorination of this waste was evaluated.

2. Materials and Methods

0.5 g of either PVC resin or flexible PVC were placed on a ceramic boat inside a horizontal glass-tube reactor. A total gas flow of 200 ml min^{-1} with varying compositions of 0, 25, 50 and 75 vol% steam was maintained. For each steam concentration, the reactor temperature was set to values between 150 and 250 °C, for reaction time intervals ranging from 15 to 180 minutes. The amount of chlorine captured in the iced water traps in the outlet of the reactor was analyzed using ion chromatography and the dehydrochlorination rate was calculated in relation to the initial amount of chlorine present in the sample mass: 57 wt% for PVC polymer and 28 wt% for flexible PVC. Reaction kinetics for steam dehydrochlorination of PVC resin were obtained using thermogravimetric analysis performed in helium and steam atmosphere. The structure of the residue was examined by SEM and FT-IR.

3. Results and Discussion

Steam assisted dehydrochlorination of PVC resin: Results for PVC resin showed that a steam concentration of 50 vol% results in the highest dehydrochlorination degree for all temperatures (Fig.1a). It was observed that there was a sharp increase in dehydrochlorination from 9.6 to 73.4% when the temperature increased from 210 to 230 °C, with no considerable rise afterward. Around 70% of the total dehydrochlorination occurred between 15 and 60 minutes of reaction time and only a further 10% was achieved for the

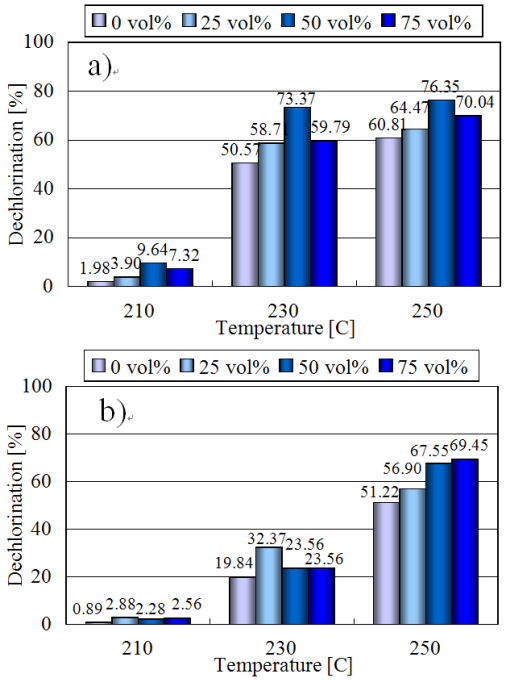

Fig.1 Dehydrochlorination after 60 minutes at variable steam fractions and temperatures for both a) PVC resin and b) flexible PVC

next 120 minutes of reaction time.

Steam assisted dehydrochlorination of flexible PVC: It was also observed that steam had a favorable effect upon dehydrochlorination. Both 50 vol% and 75 vol% contents of steam had a similar effect upon the degree of dehydrochlorination (Fig.1b). Dechlorination increased with temperature, reaching a maximum of 68% at 250 °C with 50 vol% steam concentration in 60 minutes. Almost complete dehydrochlorination was obtained after 180 minutes under these conditions. FT-IR (Fig. 2) showed a gradual increase of the OH peak in the vicinity of 3400 cm^{-1} and of the C=C peak at 1680 cm^{-1} that indicated not only an effect of the temperature but also of the steam content upon the dehydrochlorination. The decrease of the C=O peak in 1700 cm^{-1} at temperatures of more than 210 °C indicated the decomposition of the plasticizer (Fig. 2a). It was also observed that the addition of steam increased the relative occurrence of the substitution of Cl by OH-groups compared to results without steam. (Fig. 2b).

Kinetics of dehydrochlorination using steam: It is known that dehydrochlorination of PVC initially proceeds as a zero order reaction, but as dehydrochlorination progresses it tended to follow a first order reaction model[1)]. This could be observed for the steam assisted dehydrochlorination as well. Activation energy was calculated to be 120 kJ mol^{-1} for both reactions, with and without steam. This activation energy values are consistent with previously reported values for dry methods[1)], and are slightly lower in comparison to those of other dehydrochlorination methods such as NaOH/EG wet methods[2)]. Furthermore, the similar activation energies suggest that the reaction mechanisms are similar. However, the values of reaction rate constant *k* for the steam assisted dehydrochlorination were 40-50% higher compared to those of the reaction without steam at 230 °C, 240 °C and 250 °C in the first order reaction portion. Since the reaction mechanisms are similar in both reactions, it can be assumed that the steam improved the dehydrochlorination by acting as a heat and mass transfer medium.

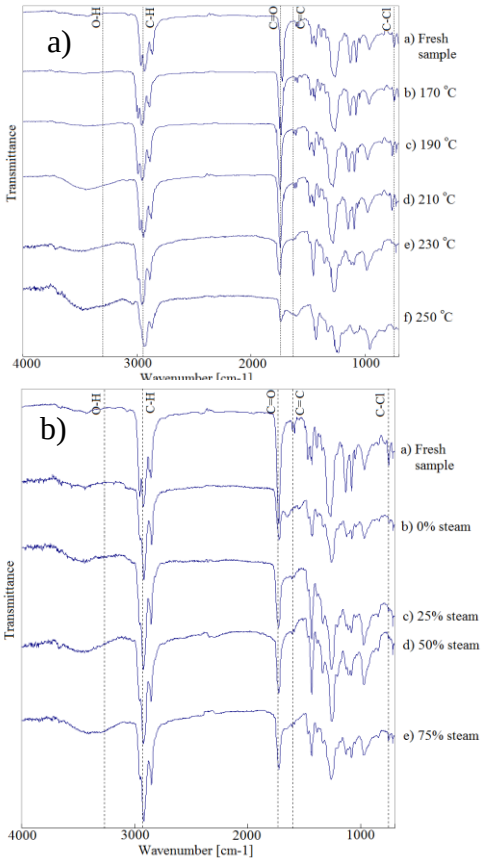

Fig. 2 FT-IR spectra of flexible PVC at various a) temperatures and b) steam contents at 250 °C. 60 minutes with 50 vol% steam.

4. Conclusions

The presence of steam in the process increased the maximum dehydrochlorination rate by about 15% for both PVC resin and flexible PVC. Furthermore, the reaction kinetics study indicated that values of *k* were observed to be 40-50% faster when steam was present. According to these results, the use of steam dehydrochlorination as a pretreatment for the recycling of PVC materials has benefits over dry processing techniques such as thermal decomposition, while offering additional benefits for targeted waste streams like flexible PVC used for medical purposes. The higher degree of dehydrochlorination provides a material better for posterior recycling. The faster reaction allows a higher volume of material to be processed in the same amount of time. As for sterilization, even though the increased processing temperatures alone can achieve this effect, the steam was observed to act as an effective heat and mass transport medium. This affects the heat distribution in the waste positively, thus assisting the effective sterilization of the material.

References

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