CHEMICAL MODIFICATION OF PVC USING Na_2S

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Abstract: The recycling of poly(vinyl chloride) (PVC) is one of the important issues in the treatment of waste plastics. In order to improve the recycling, developing new recycling techniques is necessary as well as dehydrochlorination. We already found that PVC can be dehydrochlorinated using a wet process in NaOH/ethylene glycol solution which is more effective than dry dehydrochlorination processes.

Based on the wet process, we examined the chemical modification of PVC by nucleophilic substitution in order to upgrade waste PVC. Cl was substituted in solution by several nucleophilic agents, changing the properties of PVC. The effect of the reaction of PVC in Na_2S/ethylene glycol solution at 170 ℃ was a dehydrochlorination rate of 60 % and a substitution yield of 25 %. The SEM-EDX mappings and the elementary analysis of the product indicated that the process led to the cross-linking of PVC by sulfur.

1. Introduction

Every year megatons of waste PVC are accumulate in Japan, however, only 35 % of the waste PVC has been recycled. In order to improve the recycling, it is necessary to develop new recycling techniques as well as dehydrochlorination. It was already known that PVC can be dehydrochlorinated using a wet process in aqueous NaOH [1,2] or NaOH/ethylene glycol (EG) [3] solution under these conditions, which are milder and more effective than those of dry processing, due to the nucleophilic substitution of Cl^- by OH^-, additional to the elimination of HCl. Based on the wet process, we research the chemical modification of PVC by nucleophilic substitution and developed new polymers with new functional groups in order to upgrade waste PVC during recycling. The upgrade during the recycling of PVC is expressed by Eq. (1).

$$\left[CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n + n\,Nu^- \longrightarrow \left[CH_2 - \underset{\displaystyle Nu}{\underset{|}{CH}} \right]_n + n\,Cl^- \quad (1)$$

The Cl is substituted by the dissolved Nu. In this study, we examined chemical modification of PVC using sulfur-containing dianions like S^{2-}. This process is expected to lead to the cross-linking of PVC and new properties of PVC.

2. Experimental

The examined nucleophiles (Nu) were Na_2S, $Na_2S_2O_3$, and Na_2SO_3. 1.0 g of PVC powder was added to 50 mL of Nu/H_2O or Nu/EG solution in a 100 mL flask. The molar Nu/Cl ratio was 1.0-4.0. The aqueous and EG solutions were stirred at 80 ºC and 150-190 ºC, respectively, under a N_2 flow of 100 mL/min. After cooling the reactor with water, the reactant was filtered, washed with deionized water, and dried under reduced pressure. The solid was analyzed by SEM-EDX mapping and its composition was determined by elemental analyses. The chloride concentration of the filtrate was determined by ion-chromatography.

3. Results and discussion

3.1 Dehydrochlorination of PVC in a dianionic solution

Fig. 1 shows the effect of different nucleophiles on the dehydrochlorination of PVC in aqueous solution. The dehydrochlorination of Na_2S/H_2O was 2.5% after 24 h. Both $Na_2S_2O_3$ and Na_2SO_3did not show any effect on the dehydrochlorination after 24 h reaction time.

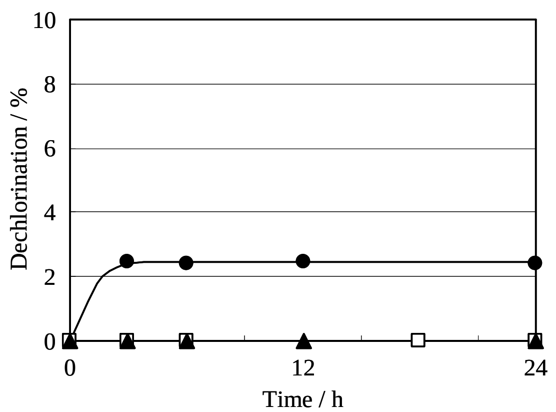


Fig.1 Degree of dechlorination of PVC powder in Nu/H_2O solution at 80℃, [Nu]/[Cl]=4: (●)Na_2S/H_2O; (□)$Na_2S_2O_3/H_2O$;(▲) $Na_2S_2O_3/H_2O$

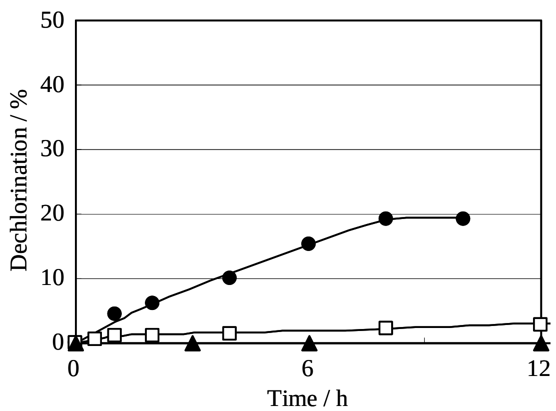


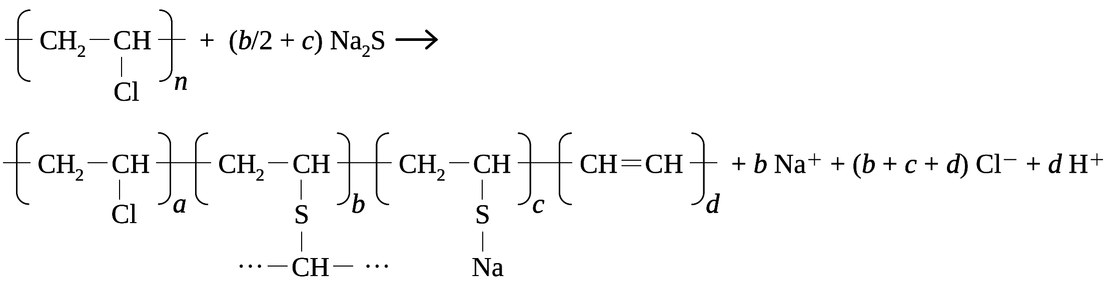
Fig.2 Degree of dechlorination of PVC powder in Nu/EG solution at 190℃, [Nu]/[Cl]=4:(●)Na_2S/EG; (□)$Na_2S_2O_3$/EG;(▲) $Na_2S_2O_3$/EG

The dehydrochlorination in EG-solution was accelerated compared with that in water (Fig. 2). The presence of Na_2S and $Na_2S_2O_3$ the dehydrochlorination reached 19.1 % and 4.6%, respectively, while Na_2SO_3 remained ineffective. These results reflect the strengths of nucleophilic reactivity in the order $Na_2S > Na_2S_2O_3 > Na_2SO_3$.

3.2 Structure of PVC modified in Na_2S/EG solution

The substitution of PVC is expressed by Formula (1). Chlorine is substituted by the dissolved Nu. In case of Na_2S, however, various structures can be formed (Formula (2)).

Besides unreacted chlorine, remaining after the substitution (*a*), cross-linked sulfur (*b*), thiolate groups (*c*), and double bonds (*d*) are observed.



(2)

The yields of the substitution of Cl by S^{2-} and the double bonds obtained by the elimination of HCl are calculated by the percentages of the different groups. The dehydrochlorination ratio is therefore expressed by the percentage of ($b + c + d$) to n.

Fig. 3 shows the SEM and the Cl, S, and Na-mapping images, obtained by EDX from the modified PVC. For Fig. 3, Cl and S were observed in the modified PVC; however, Na was not observed. This indicates that little thiol was formed, and S was mainly present in its cross-linked form ($c = 0$).

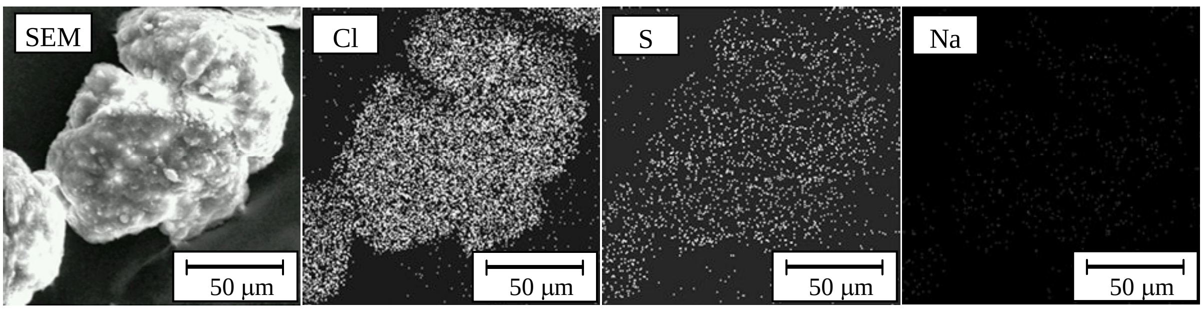


Fig.3 SEM and EDX Cl,S,and Na-mapping images of PVC modified in Na_2S/ED solution

Fig. 4 shows the ratios of the different reactions, which modified the PVC under several reaction conditions. Elementary analysis was used in order to calculate the ratios of the cross-linked S and the thiol groups. The substitution (F_S) and elimination (F_E) ratios in Fig. 4 were calculated according to the following equations.

$$F = [1 - 2 \times (\mathrm{Cl} / \mathrm{C})] \times 100$$

$$F_E = [3 - 2 \times (\mathrm{H} / \mathrm{C})] \times 100$$

$$F_S = F - F_E$$

where F refers to the percentage of dehydrochlorination. Assuming S was solely present in the form of thiols, the substitution ratio ($F_{S,\, b=0}$) is calculated according to the following equations:

$$F_{S,\, b=0} = [2 \times (\mathrm{S} / \mathrm{C})] \times 100$$

Assuming S formed only cross-linked structures, the substitution ratio ($F_{S,\ c\ =\ 0}$) is calculated according to the following equations:

$$F_{S,\,c=0} = [2 \times (2S / C)] \times 100$$

According to Fig. 4, F_S is in a close agreement with $F_{S,\,c=0}$, while $F_{S,\,b=0}$ is not able to explain the substitution ratio, indicating that the substitution of Cl^- by S^{2-} led mainly to the cross-linking of PVC by sulfur. This corresponds with the results from the EDX mappings.

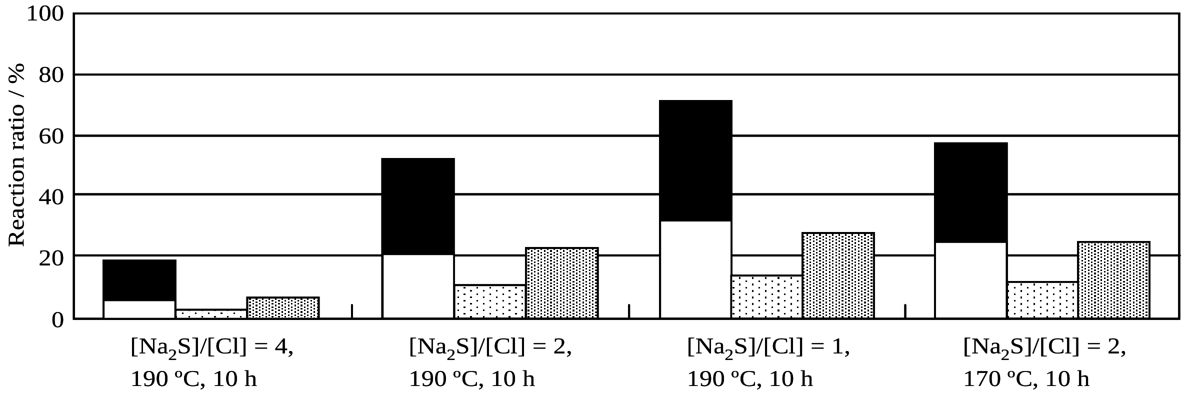


Fig.4 Reaction ration of PVC modified in Na_2S/EG solution in several reaction conditions;( )substitution(F_S,[(b+c)/n]×100);( )elimination(F_E,(d/n)×100); ( )un-cross-link($F_{S,b=0}$,(c/n)×100at b=0);( )cross-link($F_{S,c=0}$,(b/n)×100at c=0)

3.3 Control of the reaction ratio of PVC during the modification with Na_2S

The reaction conditions have a strong influence on the modification. Depending on the purpose of use, different ratios between the reactions taking place might be required. Fig. 5 shows the effect of temperature on the modification of PVC by Na_2S. The yeilds of the dehydrochlorination at 130 ºC, 150 ºC, 170 ºC, and 190 ºC were 8.6 %, 47.6 %, 57.2 %, and 52.7 %, respectively. This behaviour is unusual, since in general the dehydrochlorination ratio increases with the temperature. However, S^{2-} is oxidized at high temperatures by oxygen, dissolved in the EG. The formation of SO_4^{2-} and $S_2O_3^{2-}$ - ions with a weak nucleophile character - reduced the dehydrochlorination efficiency at high temperatures. The ratios between the substitution and the elimination were 0.09, 1.29, 0.81, and 0.68 at 130 ºC, 150 ºC, 170 ºC, and 190 ºC, respectively, resulting in the highest selectivity for the substitution at 150 ºC.

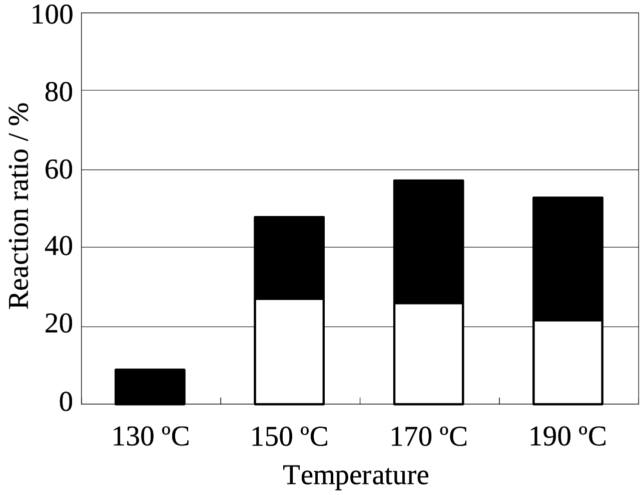


Fig.5 Effect of temperature on the reaction of PVC in Na_2S/EG solution,[Na_2S]/[Cl]=2,10h:( )substitution;( )elimination

Fig. 6 shows the effect of the Na_2S concentration on the modification of PVC at 190 ºC. The yields for dehydrochlorination were 71.5 %, 52.7 %, and 19.2 % for the molar S/Cl ratio of 1, 2, and 4, respectively. In general, the dehydrochlorination of PVC increases with an increasing Nu concentration. The vice versa effect of S^{2-} might be cause by cross-linking of PVC chains at the surface. By this, a deeper penetration of the PVC particle by the solvent and the nucleophile is prevented, limiting the dehydrochlorination to the surface. The ratios between the substitution and the elimination were 0.82, 0.68, and 0.45 for molar S/Cl ratio of 1, 2, and 4, respectively. Therefore, the selectivities of the substitution (substitution/dechlorination ratio) were 0.45, 0.41, and 0.31, respectively.

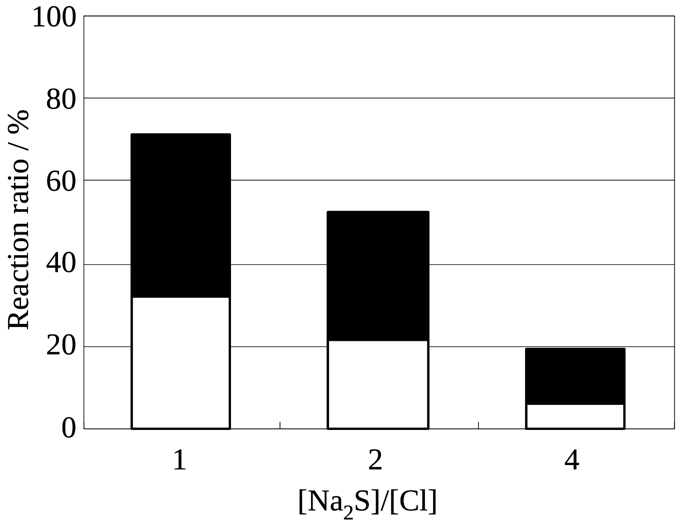


Fig. 6 Effect of Na_2S concentration on the reaction of PVC in Na_2S/EG solution at 190 ºC, 10 h: ( )substitution; ( )elimination

4. Conclusions

The substitution of PVC was investigated in a dianionic solution. Na_2S/EG solutions were effective in modifying PVC, leading to the cross-linking of PVC by sulfur. The behavior of S^{2-} differed from nucleophiles, used for the modification of PVC due to oxidation of S^{2-} by oxygen, dissolved in EG, and the hindered penetration of the PVC particles by the solvent due to the cross-linking of PVC chains at the particle surface.

References

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