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폴리염화비닐(PVC)의 열안정성에 제올라이트가 미치는 영향

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Effects of Zeolites on Thermal Stability of Poly(vinyl chloride)

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Abstract: The effects of zeolite on the thermal stability of poly(vinyl chloride) (PVC) were investigated by the static thermal stability test, pyrolysis experiment and ultraviolet spectrum. The results showed that the porous zeolite could absorb hydrogen chloride (HCl), which suppressed the catalysis of HCl on thermal degradation of PVC, thus improved the thermal stability of PVC. The oxidizing acid which was loaded on zeolite had oxidated on the double bond that formed during the dehydrochlorination of PVC. This process could prohibit the growth of the conjugated polyene and improved the color of PVC. Hence, zeolite might be possible to come up with a high performance thermal stabilizer.

Keywords: zeolite, poly(vinyl chloride), stability, oxidizing acid, double bond.

Introduction

Poly(vinyl chloride) (PVC) resins, a type of thermoplastic material, which are widely used due to their non-flammable nature, good performance and low price. However, PVC resins have poor thermal stability which results in severe discoloration and mechanical properties.[1,2] The degradation of PVC proceeded by a dehydrochlorination process results in the formation of long conjugated double bonds or polyene sequence (-CH=CH-)n and the release of gaseous HCl.[3] To prevent undesirable degradation of PVC, a number of chemicals can be used as thermal stabilizers, such as metal soaps, organotin, organic stabilizers, inorganic stabilizers (zeolite,[4,5] hydrotalcite[6]).

Zeolites have a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement that permits ion exchange and reversible dehydration,[7] Zeolite can exchange Na^+ ions by H^+ ions.[8] Zeolites contain pores can absorb HCl.[9] In recent years, zeolite has been reported to be effective co-stabilizer to Ca/Zn stabilizer for PVC. Ca/Zn heat stabilizer is composed of zinc, calcium soap, chelating agent, zeolite and other co-stabilizer.[10] Savrk[11] performed statistically designed experiment to investigate the effect of $ZnSt_2$ and zeolite on thermal stability of PVC regarding temperature. The combination of higher alkalinity and the pore structure of zeolite was believed to be significantly responsible for their thermal stabilization.[12]

PVC is required to have long-term stability and to keep good initial color. Zeloites similar to hydrotalcites shows long-term stability, but initial color fading. So, this study aims to investigate the effect of zeolite on the thermal stability of PVC and the improvement of initial color fading of PVC by loading of the oxidating acid on zeolite.

Experimental

Materizals. PVC SG-5 resin was supplied by the Yibin Tianyuan Reagent Co., Ltd, China. Na-A zeolite powder with average size of 2-5 μm was purchased from the PQ Co.,USA.

Activation of Zeolite. A certain amount of zeolite was immersed in a certain concentration of oxidizing acid for 2 h, then filtered and dried in oven at 90 °C. The changes of the specific surface area of zeolites were measured by N_2 adsorption-desorption isotherms. The morphology of zeolites were observed by scanning electron microscope (SEM).

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Test and Characterization.

Congo Red Measurement: Congo red values were determined by PVC, PVC/zeolite and PVC/activated zeolite samples in an airtight test tube heating up to 180 ºC. A strip of Congo red test paper was placed at the top of the test tube to record the colour change time, which was referred as the stability time.

Oven Heat Stability Test: Mixture of PVC containing zeolites were made into sheets by a double rolling mill. The rectangle sheets of 1 cm×1.5 cm in size were placed in an oven controlled at 180.0±2 ºC in temperature. Then, sheets were taken out to observe color change by a CM-2006d spectrophotometer in every 10 min interval.

Thermal Decomposition Experiment:[13] Thermal decomposition of PVC, PVC/zeolite and PVC/activated zeolite were examined at 200±2 ºC. The decomposition products were absorbed by deionized water, then its conductivity at different times was measured and the curve of the conductivity versus time was drawn.

Ultraviolet Spectrum Analysis: Thermal decomposition products of PVC, PVC/zeolite and PVC/activated zeolite at 200±2 ºC were absorbed by ethanol and analysed by the absorbance scanned using UV-7504 spectrophotometer from Shanghai XINMAO Co.,Ltd ranging from 200 to 300 nm in wavelength.

Results and Discussion

Effect of Zeolites on Thermal Stability of PVC. Thermal Stability: The results of the thermal stability of PVC/zeolite and PVC by Congo red test at 180 ºC are shown in Figure 1.

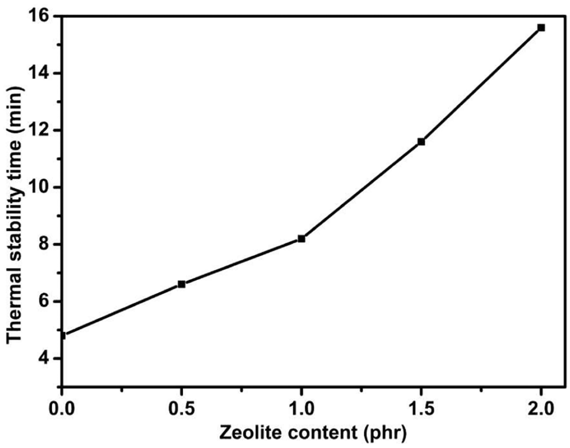


Figure 1. Effect of zeolites content on static stability time of PVC at 180 ºC.

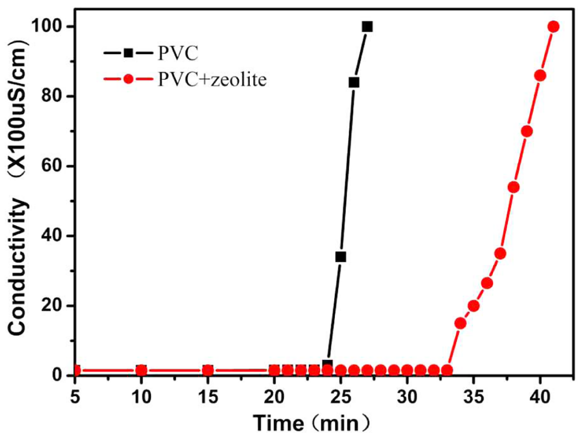
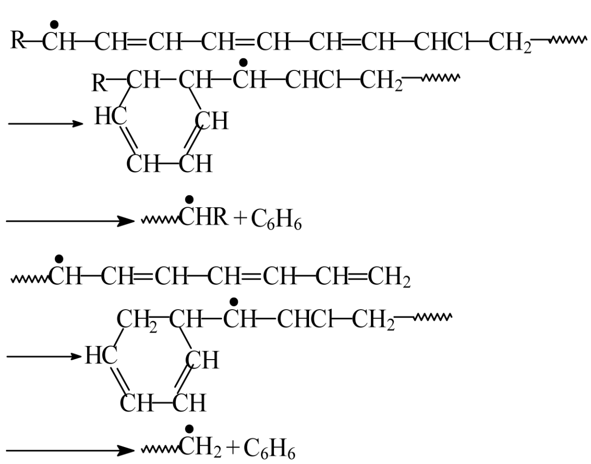


Figure 2. Change of the conductivity of aqueous solution *vs*. time at 200 ºC for decomposition of PVC and PVC/zeolites.

The static thermal stability of PVC increases with the increasing of the content of zeolites, due to the increasing of the absorption ability of zeolites on HCl, accordingly, the samples with 0.5 phr zeolite in content were used in the later experiments.

Thermal Decomposition Curve of PVC: Thermal decomposition curves of PVC and PVC/zeolite at 200 ºC are shown in Figure 2. The induction time[11] of PVC/zeolite was prolonged long about 15 min compared with that of PVC. Zeolites in PVC/zeolite apparently improve the thermal stability of PVC. Which implies zeolite would absorb HCl. This is because zeolite could exchange Na^+ ions by H^+ ions, at same time zeolite contains pores that can adsorb HCl.[11] In addition to HCl, benzene were also produced in thermal decomposition of PVC, which was caused by the cyclization of conjugated polyene, the mechanism was proposed as followings:[14]



The content of conjugated polyene produced during thermal degradation of PVC can be determined by the content of ben-

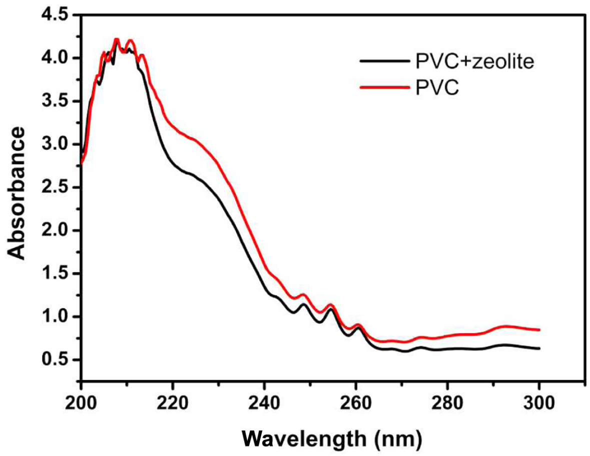
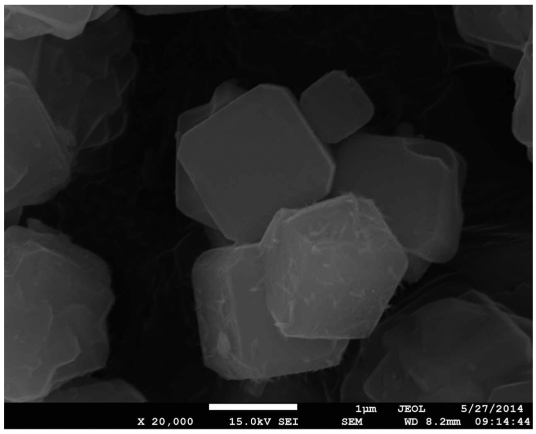


Figure 3. UV-VIS spectra of PVC and PVC/zeolite.

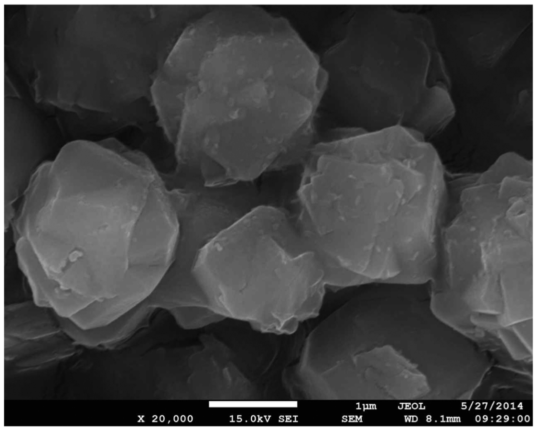
zene indirectly. Thermal decomposition products of PVC and PVC/zeolite were absorbed by ethanol, and the solvent was analysed by ultraviolet spectrum to study the effect of zeolite on thermal decomposition of PVC. Ultraviolet spectrum curves shown in Figure 3 indicates that thermal decomposition products of PVC/zeolite and PVC are quite similar. The absorption peaks are mainly appeared at 210 and 254 nm. The appearance of five absorption peaks at around 254 nm prove the existence of benzene, while the absorption at 210 nm was the E2 absorption band of benzene, in addition, the absorption peaks around at 210 nm being attributed to the presence of a certain amount of short chain conjugated polyenes.[15,16] It can be seen that the UV curve of PVC/zeolite is consistent with that of PVC when compared the absorption peaks at around 210 and 254 nm, respectively. Thus it can be concluded that the presence of zeolite may surely prevent the thermal decomposition of the PVC.

Effect of Activated Zeolite on Thermal Stability of PVC. Zeolite Activation: The acid treatment of zeolite not only removes the impurities and insoluble substance that obstruct the cavity and hollow of zeolite, but also promotes to carry the oxidation acid into the cavity and the hollow of the zeolite. The carried acid can be released under the applied heat to make the zeolite functional. Figure 4 is the SEM pictures of treated (a) and untreated (b) zeolite. The Na-A zeolites is made of silica and alumina tetrahedron to form three-dimensional skelton structure compound which belongs to the cubic crystal system. Its particle size is about 2-5 μm in diameters. SEM micrograph of activated zeolites shows more irregularity in shape, which results in the increasing of the specific surface area.

The changes of the specific surface area of zeolites can be seen from Figure 5, the specific surface area of zeolite is 10.6 m^2/g, however, the activated zeolites is increased to 62.2 m^2/g, the adsorbed volume of the activated zeolite is



(a) Zeolite



(b)Activated Zeolite

Figure 4. SEM micrograph of zeolites and activated zeolites.

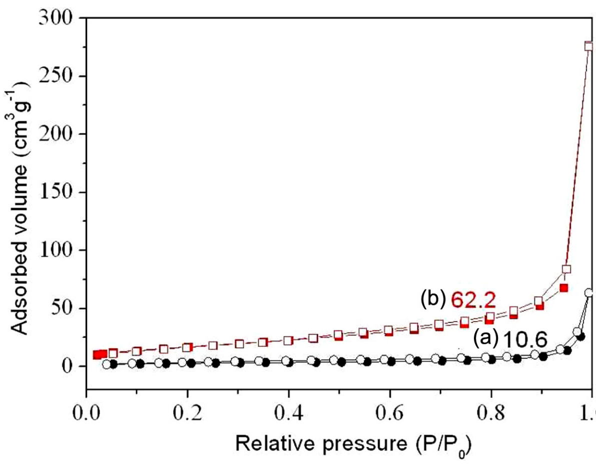


Figure 5. N_2 adsorption-desorption isotherms of zeolites: (a) zeolite; (b) activated zeolite.

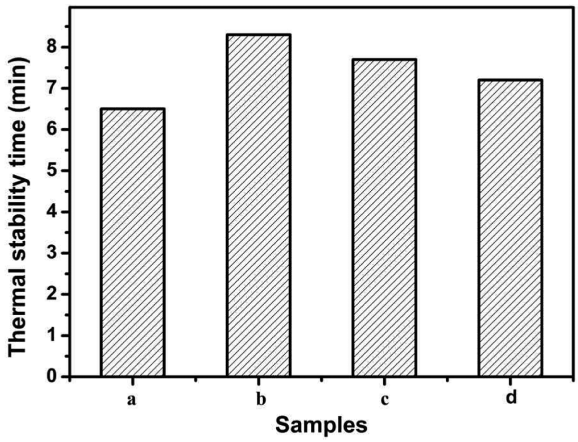


Figure 6. Effect of zeolites on the thermal stability of PVC: (a) PVC+zeolite; (b) PVC+zeolite activated by 1% acid; (c) PVC+zeolite activated by 2% acid; (d) PVC+zeolite activated by 3% acid.

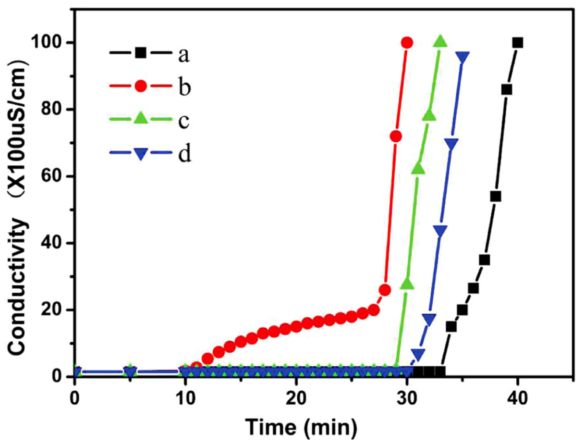


Figure 7. Thermal decomposition curves of PVC/zeolite and PVC/activated zeolite: (a) PVC+zeolite; (b) PVC+zeolite activated by 1% acid; (c) PVC+zeolite activated by 2% acid; (d) PVC+zeolite activated by 3% acid.

larger than the zeolite.

Effect of Activated Zeolite on the Thermal Stability of PVC: As shown in Figure 6, the thermal stability of PVC/activated zeolites is higher than that of PVC/zeolite. The acid removes the impurities and the insoluble substances that obstruct the cavity and hollow of zeolite for the HCl absorption sites.

The release rate of HCl of PVC/ activated zeolite is higher than that of PVC/zeolite (see Figure 7). This is due to the oxidizing acid loaded on the zeolite releases from zeolite and catalysis the thermal decomposition of PVC when zeolite subjected to an elevated temperature.

The colour change of PVC/activated zeolites during thermal decomposition is exhibited in Figure 8. The colour of PVC/activated zeolites changes from colorless → pale yellow → brown → black, and the colour of PVC/zeolite does from colorless → pale yellow → yellow orange → red orange → red → brown, Hence the activated zeolite improves initial colour change in the pyrolysis process.

At the same time, the color difference Δ*E* of the PVC/activated zeolites from 0 to 50 min is lower than that of the PVC/zeolites as given in Figure 9, The reason is that oxidizing acid released from zeolite and oxidize the double bond, which hinders the formation and the growth of conjugated polyene. Thus the colour change of the PVC is prevented.

The thermal decomposition products of PVC/activated zeolite and PVC are shown in Fgure 10. When we compare the five characteristic absorption peaks of benzene at 210 and 254 nm, the relative intensity of ultraviolet absorption of PVC/activated zeolite is lower than that of PVC. The content of the short chain of the conjugated polyenes and benzene was decreased. Because the released oxidizing acid oxidate the double bond which being formed in the dehydrochlorination process of PVC, inhibited the formation and the growth of conjugated polyenes. The decreasing of the amount of short chain conjugated polyenes and benzene is quite important mechanism of the improvement of the initial color fading of PVC. zeolite might be good candidate material to improve

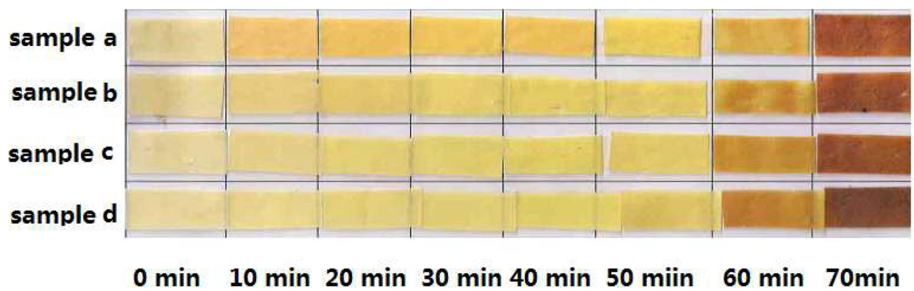


Figure 8. Colour change of PVC sheets with time at 180 ℃: (a) PVC sheets containing zeolites; (b) PVC sheets containing zeolites activated by 1% acid; (c) PVC sheets containing zeolites activated by 2% acid; (d) PVC sheets containing zeolites activated by 3% acid.

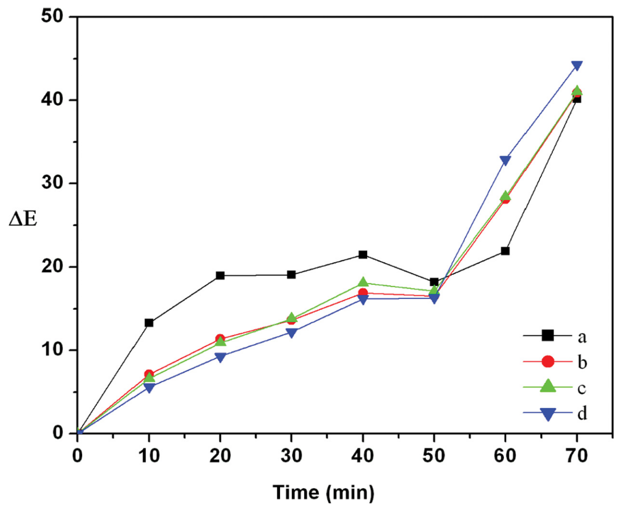


Figure 9. Color difference of PVC sheets with time at 180 °C: (a) PVC sheets containing zeolites; (b) PVC sheets containing zeolites activated by 1% acid; (c) PVC sheets containing zeolites activated by 2% acid; (d) PVC sheets containing zeolites activated by 3% acid.

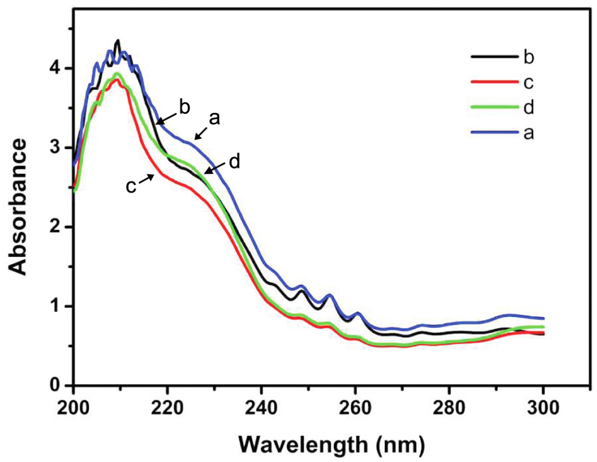


Figure 10. UV-vis spectra of PVC and PVC/activated zeolite: (a) PVC+zeolite; (b) PVC+zeolite activated by 1% acid; (c) PVC+zeolite activated by 2% acid; (d) PVC+zeolite activated by 3% acid.

thermal stability of PVC and maintain the stability in colour change of the PVC pyrolysis process.

Conclusions

Based on the extensive analysis conducted in this study, it could be concluded: ① The porous zeolite could absorb HCl, which suppressed the catalysis effect of HCl on degradation of PVC, and improved the thermal stability of PVC. ② The oxidizing acid loaded on zeolite which is released by heating up, oxidats the double bond. Conseqencely, the formation and the growth of conjugated polyene is hindered. This results in the improvement of the initial colour change of PVC.

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