Synthesis of carbon materials by the short-term mechanochemical activation of polyvinyl chloride

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Abstract

Mechanochemical activation of PVC in a high-energy centrifugal-planetary mill was shown to increase its reactivity in dehydrochlorination under the action of bases. Thus modified PVC is capable of low-temperature carbonization and can form a carbon material even at the temperatures below 400 °C.

1. Introduction

Chloropolymer materials are widely employed in industry, the world production of the most abundant carbochain chloropolymer – polyvinyl chloride (PVC) – reaches 35 million tons per year [1]. Unqualified burning of chlorine-containing wastes inevitably leads to dioxin-like compounds, which are the strongest toxicants and belong to the group of most harmful environmental poisons (the so-called “dirty dozen”). To prevent a release of such compounds, it is necessary to develop methods for chlorine removal from polymers without high-temperature treatments.
The most popular approaches to the treatment of chloropolymer wastes are pyrolysis, mechanochemical removal of chlorine and dechlorination of polymer in solutions; however, such technologies cannot prevent the formation of high-toxic and corrosive substances and make it necessary to perform long-term treatments.

Our recent study [2] showed that the alkaline dehydrochlorination of carbobain chain chloropolymers with an increased (with respect to PVC) content of chlorine (above 60 wt. %), in particular the chlorinated PVC, polymers and copolymers of vinylidene chloride, results in the formation of reactive polymers with conjugated system (PCS) – polychlorovinylenes. Owing to the increased reactivity of the obtained PCS, they are converted into carbon species already at the temperatures below 400 °C [3].

The application of the indicated approach to processing of the most tonnage chloropolymer – PVC – is hindered by a low solubility of PVC and by the formation of low reactive polyvinylenes upon its dehydrochlorination instead of polychlorovinylenes that contain mobile chlorine atoms.

This work elucidates the possibility of mechanochemical activation of PVC to intensify its dehydrochlorination and increase the reactivity of the produced polyvinylenes in further thermal transformations.

2. Experimental

In the study, the initial polymeric material was represented by polyvinyl chloride (PVC) suspension, PVC-S-SI-70, manufactured according to Specs 2212-012-46696320-2008 by JSC Sayanskhimplast (Sayansk).

Mechanical treatment of PVC was performed in an AGO-2 high-energy centrifugal-planetary mill (a 5 g sample, a 60 g acceleration of milling balls, and a power of 100 W/g supplied by the balls). The treatment conditions (duration and introduction of additives) were chosen so as to prevent adhesion of the polymer particles.

For dehydrochlorination of PVC, a polymer sample was distributed in the calculated amount of dimethyl sulfoxide (DMSO) to obtain 1 % wt. dispersions by ultrasonic treatment with the use of an immersion ultrasonic disperser (frequency 23 kHz, power 100 W, contact time 10 min). This was followed by the addition of potassium hydroxide (a twofold excess over the theoretical amount needed for a complete removal of HCl). The synthesis was carried out at 20 °C for 6 h under constant stirring. The process was controlled potentiometrically, the resulting product was filtered, washed with water in a Soxhlet apparatus to remove Cl– ions from the filtrate, and dried at 100 °C.

Sampling was made each hour in the course of dehydrochlorination. A 1 ml sample was placed in a 25 ml volumetric flask, and the contents of alkali and chloride ions in the resulting aqueous solution were found by potentiometric titration. Potentiometric titration of the medium was carried out with a Multitest IPL-112 potentiometer using the system “silver electrode – silver-chlorine electrode” for chloride ions, and a glass electrode for hydroxide ions. Aqueous solutions of hydrochloric acid (0.05 n) and silver nitrate (0.02 n, 0.1 n) were used as titrants.

Carbonization of the synthesized samples was performed in a tube furnace SNOL 7.2/1100 in flowing CO2 at a gas flow rate of 5 cm3/min in two steps: at 200 °C for 2 h and at 400 °C for 2 h.

Raman spectra were recorded on a DXR Smart Raman (ThermoScientific) dispersion spectrometer equipped with an attachment for recording the backward scattering in a range of 50-3400 cm-1. The exciting laser wavelength was 633 nm; laser power, 1 mW.

The morphology of the synthesized materials was studied by scanning and transmission electron microscopy (SEM and TEM) using, respectively, a JSM-6610LV JEOL electron microscope with an energy dispersive X-ray spectrometer INCAx-act (Oxford Instruments) and an EM 2100 JEOL high resolution transmission electron microscope (accelerating voltage of 200 kV and crystal lattice resolution of 0.14 nm) with an INKA 250 (Oxford Instruments) energy dispersive X-ray spectrometer.

3. Results and discussion

The application of mechanochemical action to accelerate chlorine removal from PVC is reported in the literature. Usually it is a relatively long-term treatment in the presence of main agents able to bind HCl, such as hydroxides of alkali metals [4], Ca oxides, hydroxides and salts [5-7], as well as natural materials containing calcium carbonate [8].
In this work, a short-term mechanical activation in a powerful high-energy centrifugal-planetary mill was used as a step of PVC pretreatment aimed to increase its reactivity during dehydrochlorination in an alkaline medium.

Our earlier work on mechanical treatment of polymers [9] demonstrated that the addition of small amounts of organic solvents facilitates the formation of a finely dispersed state of a substance. This may be attributed to manifestation of the Rehbinder effect, which is related to a reduction in the hardness of a material and facilitates its dispersion upon contacting with a liquid medium.

In our work, the optimal results of PVC mechanical activation were obtained when PVC was treated in the presence of dimethyl sulfoxide and ethanol, the amount of which constituted 10% wt. of the polymer amount. A series of experiments showed that the optimal activation time is 20 s (a longer treatment led to adhesion of the polymer particles).

According to Raman spectroscopy data, mechanical activation of PVC under the chosen conditions does not change the polymer structure. The spectrum of the mechanical treatment product, similar to the spectrum of the initial polymer, shows high-intensity Raman bands at 635 and 695 cm⁻¹, which assign to stretching vibrations of C-Cl bonds. An intense Raman band at 2916 cm⁻¹ is also observed, which corresponds to stretching vibrations of C-H bonds in the -CH₂- structural fragment (Fig. 1).

A SEM study of the materials showed that the initial PVC is represented by the round 1-5 μm particles and by the larger ones that form round grains with the size of 100 μm (Fig. 2a, c). After mechanical treatment, the surface of the primary PVC particles becomes smoother; however, their linear size does not show substantial changes and is equal to 200-500 μm (Fig. 2b, g).

Energy dispersive X-ray spectroscopy data confirmed that mechanical activation in the presence of organic solvents produces no significant changes in the chemical composition of PVC, the content of C and Cl remains at a constant level.

Conditions of dehydrochlorination of mechanically activated PVC in the presence of alkali were chosen so as to obtain its stable dispersions in DMSO, which, according to our earlier study [10], is a preferable medium for dehydrochlorination of chloropolymers. This solvent complies with the requirements of accessibility, low toxicity and high reaction rate in the temperature range of 20–60 °C.
The particles of mechanically activated PVC were stabilized in the DMSO medium by ultrasonic treatment. It should be noted that ultrasonic treatment in DMSO does not lead to the formation of stable dispersions in the case of PVC not subjected to mechanical activation.

Dehydrochlorination was carried out in PVC dispersions at the polymer concentration of 1 % wt. for 6 h at room temperature and a PVC – potassium hydroxide weight ratio of 1:1.

According to potentiometric titration of the reaction medium upon PVC dehydrochlorination, the materials that were mechanically activated for 20 s have already a much higher reactivity in dehydrochlorination. However, an extension of mechanical activation time to 40 s further accelerates the process and provides a much higher degree of dehydrochlorination (Fig. 3).

Thus, in the case of PVC mechanically activated for 40 s, a sharp drop of the OH– concentration in the reaction medium is observed already 10 min after the interaction with alkali, and in 1 h the reaction virtually terminates. Therewith, for the sample not subjected to mechanical activation, such drop of the OH– concentration is not reached even in 6 hours.
Fig. 3. Concentration of OH ions versus the time of PVC dehydrochlorination in DMSO under the action of KOH: (1) – non-activated PVC, (2) – after 20 s of mechanical activation, and (3) – after 40 s of mechanical activation.

Raman spectroscopy data for dehydrochlorination products of mechanically activated PVC (Fig. 4, spectrum 1) indicate the formation of conjugated double bond systems in the polymer with the corresponding intense narrow Raman bands at 1109 and 1491 cm$^{-1}$ [11].

Thus, potentiometric titration and Raman spectroscopy data confirmed that the short-term mechanical activation in a high-energy centrifugal-planetary mill efficiently increases the reactivity of PVC upon its dehydrochlorination in the presence of alkali in the DMSO medium.

Polyvinylenes produced by dehydrochlorination were heat treated in an inert medium via two steps: at 200 °C for 2 h and at 400 °C for 2 h, according to the earlier developed technique [10]. Changes in the structure of materials that accompanied their thermal transformations are illustrated by Raman spectroscopy data (Fig. 4).

Fig. 4. Raman spectroscopy data: (1) – polyvinylene obtained by dehydrochlorination of PVC, (2) – after heat treatment at 200 °C for 2 h, (3) – after heat treatment at 200 °C for 2 h and at 400 °C for 2 h.
No Raman bands typical of polyene chains are observed in the spectrum of the products obtained by heat treatment of polyvinylenes at 400 °C. However, there are Raman bands at 1359 and 1593 cm\(^{-1}\) (Fig. 4, spectrum 3), which are typical of carbon materials. Thus, Raman bands at 1593 cm\(^{-1}\) are assigned to stretching vibrations of C=C bonds in conjugated aromatic compounds, the bands at 1359 cm\(^{-1}\) are attributed to the defect structure of carbon material.

According to energy dispersive X-ray spectroscopy data, the chlorine content in the products of polyvinylene heat treatment in the temperature range up to 400 °C is as low as 0.6 % wt.

4. Conclusion

Mechanochemical activation of PVC in a high-energy centrifugal-planetary mill increases the reactivity of PVC in dehydrochlorination under the action of bases. Thus modified PVC is capable of the low-temperature carbonization and forms a carbon material even at the temperatures below 400 °C.

This can be used as a basis to develop high-performance technologies for processing of PVC and its wastes into marketable carbon materials that are applicable in various fields of industry (adsorbents, catalyst supports, electrode materials, fillers for polymers, and others).

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