

Chemical Recycling of Poly(vinyl chloride): Application of Partially Dehydrochlorinated Poly(vinyl chloride) for Producing a Chemically Modified Polymer

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ABSTRACT: Poly(vinyl chloride) (PVC) pipes were chemically modified to produce a sulfonated polymer with dehydrochlorinated PVC samples as intermediates. Two intermediates were formed: (1) partially dehydrochlorinated PVC with long sequences of conjugated double bonds and (2) the product of the partial dehydrochlorination of PVC and the nucleophilic substitution of chlorine by hydroxyl groups. The IR spectra showed that the dehydrochlorinated samples were heterogeneous materials, showing different proportions of elimination products, hydroxyl substitution, and partial oxidation. Samples

dehydrochlorinated with poly(ethylene glycol) with a molecular weight of 400 g/mol for 24 h and 15 min showed the highest sulfonation yield, which was related to the sulfonation mechanism occurring predominantly because of the presence of hydroxyl groups in a mixture of vinyl alcohol and vinyl chloride units. The sulfonation was confirmed by the presence of a medium-intensity band at 1180 cm⁻¹, assigned to sulfonic groups. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1474–1479, 2010

Key words: FT-IR; poly(vinyl chloride) (PVC); recycling

INTRODUCTION

Poly(vinyl chloride) (PVC) is an important nonbiodegradable thermoplastic used in several applications, including pipes, connections, wire/cable insulation, films, footwear, medical devices, and packing. This versatility is due to a wide range of additives that are incorporated into PVC resins, which modify the mechanical properties of the resulting material.

High PVC consumption, which reaches about 25 million tons per year in the world, is responsible for secondary effects that elevate waste material generation after its useful life.¹ The decrease in its thermal and mechanical properties during its useful life and exposition to environmental conditions decreases the quality of the recycled material. PVC recycling can be thermomechanical, energetic, or chemical. The first process reduces the mechanical and chemical properties because of the low thermal stability of PVC, which may cause its decomposition and dehydrochlorination.

The energetic recycling of PVC needs a high financial investment because special filters are necessary to prevent problems related to hydrochloric acid (HCl) release during the combustion process.

Chemical recycling is an alternative method for minimizing the recurrent environmental problems of PVC residues. Despite the reactivity difference between PVC and its analogous low-molecular-weight compounds, PVC can be chemically modified by nucleophilic substitution of chlorine atoms in its structure. Because of this difference, elimination products are favored, which lead to PVC dehydrochlorination and the development of conjugated double bonds. Dehydrochlorination may take place with HCl release as a result of heating, exposition to UV radiation, or chemical reaction in alkaline medium.^{2,3} Nucleophilic substitution and elimination reactions can be carried out to produce materials with new properties. However, partially dehydrochlorinated PVC can be used as an intermediate product, similarly to what is performed for the production of ion-exchange materials with poly(vinyl alcohol).⁴ One positive aspect of using dehydrochlorinated PVC as an intermediate product is the reduction of its toxicity because this process prevents the production of chlorinated organic compounds such as those produced during PVC

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combustion. Several processes have been studied for chemical modification of PVC^{2,5,6} and other petrochemical derivatives^{7,8} with the aim of reusing waste materials and producing new polymers, for example, polymer sulfonation, which can result in materials with ion-exchange characteristics. Ion-exchange materials are generally produced by the introduction of ion-exchanger groups, such as sulfonic groups. In this case, the polymer backbone works as a support to these groups. The chemical modification of synthetic polymers, such as PS cups and trays, has been successfully carried out.^{9,10} With regard to PVC, sulfonation can occur through the substitution of chlorine atoms by SO₃H or due to the electrophilic addition to the double bonds on the dehydrochlorinated material, similar to the diene electrophilic reaction.

In this study, the dehydrochlorination of PVC followed by its sulfonation was used to produce an ion-exchange resin from waste PVC pipes. The produced materials were evaluated by Fourier transform infrared (FTIR) spectroscopy and ion-exchange capacity measurements.

EXPERIMENTAL

Materials

The PVC used in this study was obtained from discarded pipes, washed with distilled water, dried at room temperature for 24 h, and stored at room temperature. Poly(ethylene glycol)s with molecular weights of 400 g/mol (PEG 400) and 1500 g/mol (PEG 1500), tetrahydrofuran (THF), ethanol, potassium hydroxide, and sulfuric acid were purchased from VETEC, were analytical-grade pure, and were used without further purification.

Dehydrochlorination

PVC dehydrochlorination was performed in a process adapted from the work of Guo et al.,^{2,11} as described in the following text.

A solution containing THF, PVC, and poly(ethylene glycol) (PEG; 20 : 1 : 2 w/w) was used. This solution was slowly poured over the surface of an aqueous KOH solution (40%, w/w). The process was carried out at room temperature, and the system was kept still for 24 h. After this period, a black film formed on the aqueous phase surface. The films were washed first with a large amount of distilled water and then ethanol and dried at room temperature. PEG 400 and PEG 1500 were used to produce the samples DPVC-A and DPVC-B, respectively.

Two other samples were produced with PEG 400 as a phase-transfer agent, and the same compositions were used to prepare DPVC-A. However, in

one of the samples, the only difference was the use of stirring (DPVC-C), whereas the other was also produced under stirring, but the reaction time was reduced to 15 min (DPVC-D).

Sample DPVC-E was prepared by the addition of a PVC/THF (1 : 20 w/w) solution dropwise in a KOH/ethanol solution (1 : 1 mol/mol), and the system was stirred for 24 h. After that, the product was washed with distilled water and ethanol to remove residual KOH and dried at room temperature.

Sulfonation

The DPVC-A, DPVC-B, DPVC-C, and DPVC-E samples were dipped in concentrated sulfuric acid for 24 h. After this period, the products were washed with distilled water and ethanol until neutralization was reached; these produced samples were SDPVC-A, SDPVC-B, SDPVC-C, and SDPVC-E, respectively.

A suspension of DPVC-D in THF was produced, concentrated sulfuric acid was added dropwise, and this system was stirred for 24 h. The produced material (SDPVC-D) was filtered, washed, and dried at room temperature.

Sample characterization

FTIR spectroscopy

PVC, dehydrochlorinated poly(vinyl chloride)s (DPVCs), and dehydrochlorinated poly(vinyl chloride)s (SDPVC) were characterized by FTIR spectroscopy to evaluate the chemical modification of the polymers. The PVC film and KBr tablets (1 : 100 sample/KBr w/w) pressed with the samples were analyzed in a PerkinElmer Spectrum 1000 infrared apparatus. The number of scans was fixed at 28 with a resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

The films produced from waste PVC pipes were analyzed by FTIR spectroscopy. The spectrum is shown in Figure 1. The main absorption bands are highlighted in Figure 1, and the assignments are presented in Table I.

Dehydrochlorination process

Dehydrochlorination is an elimination reaction in which the nucleophile attacks the hydrogen in the β -carbon and promotes the formation of double bonding when chloride is removed. Usually, elimination and substitution reactions compete with each other, and under certain conditions, elimination predominates over substitution. Elimination occurs if the nucleophile attacks the carbon bonded to the

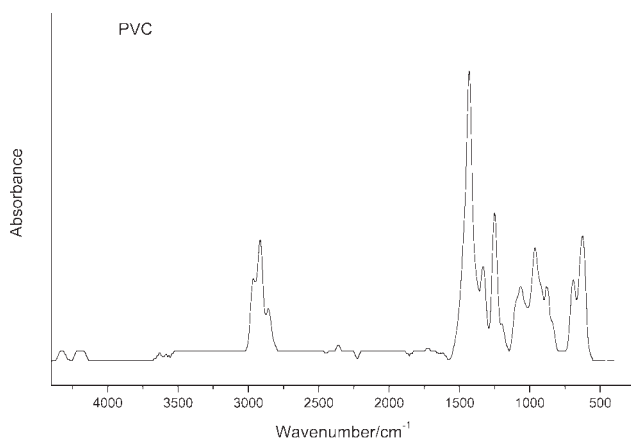


Figure 1 FTIR spectrum of the PVC membrane.

halogen instead of the hydrogen in the β -carbon. In this case, halogens are replaced by hydroxide ions.¹² Despite halogenated polymers such as PVC showing similar structures to primary low-weight halogens, some important factors affect the competition between the elimination and nucleophilic reactions; these are physical differences, such as high molecular weight, strong intermolecular interactions of the macromolecule in solution, and the use of distinct solvents for the nucleophile and polymer because of polarity differences.

The dehydrochlorination methodology was studied to produce an adequate intermediate for PVC modification. FTIR spectra for the DPVC samples are shown in Figures 2–4.

Figure 2 shows the FTIR spectra for DPVC-A and DPVC-B. The DPVC-A dehydrochlorination reaction was confirmed by the presence of new bands at 1617 and 1005 cm^{-1} . These bands were associated with double-bond formation, which indicated the occurrence of elimination reaction.^{2,11} The modification of the bands at 692 and 625 cm^{-1} was also an important confirmation of the reaction because it indicated qualitatively a decrease in the chloride content of the sample. The main FTIR band assignments for the dehydrochlorinated samples are summarized in Table II.

TABLE I
Main FTIR Absorption Assignments for the Unmodified PVC

| Wave number (cm^{-1}) | Assignment |
|----------------------------------|--|
| 2915 | C—H stretching |
| 1421 | CH_2 deformation |
| 1247 | HC—Cl angular deformation out of plane |
| 688 | C—Cl stretching |
| 624 | C—Cl stretching |

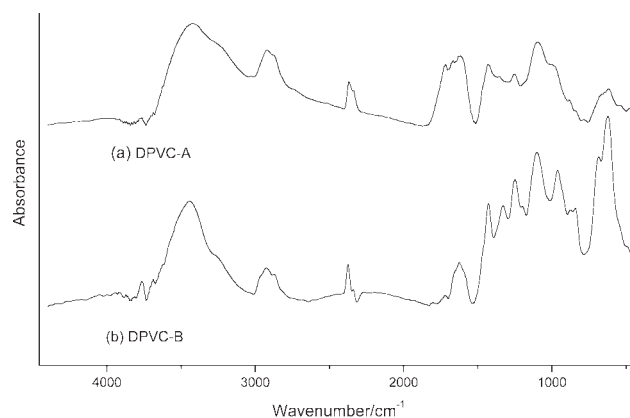


Figure 2 FTIR spectra of the dehydrochlorinated PVC: (a) DPVC-A (PEG 400) and (b) DPVC-B (PEG 1500).

Another important aspect in the characterization of this product was its color, which indicated the reaction progress because the dehydrochlorinated materials were dark. In addition to the elimination product, the process led the formation of partially substituted product, which was confirmed by the presence of an O—H stretching absorption band at 3400 cm^{-1} . This indicated the existence of a competitive process between HCl elimination and OH^- nucleophilic substitution, which led to the heterogeneous modification of PVC. The presence of a band at 1717 cm^{-1} was indicative of oxidation during chemical modification.

A similar FTIR pattern was observed for DPVC-B, shown in Figure 2(b). Despite the elimination reaction, it was possible to observe that the process was less effective for this sample in comparison to DPVC-A because the region of C—Cl stretching bands showed only little modification in relation to the unmodified PVC. Another significant difference

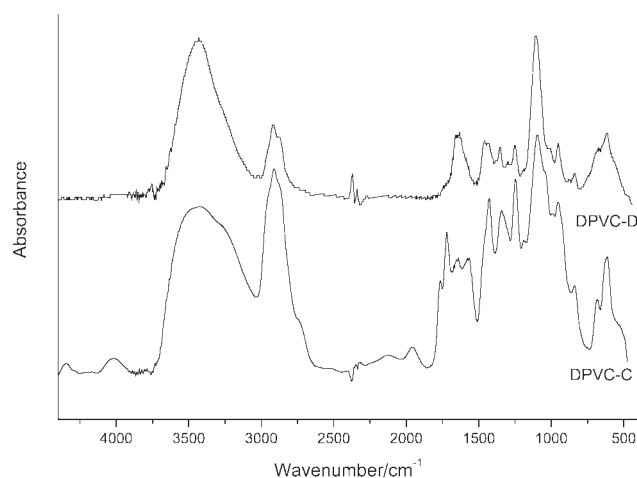


Figure 3 FTIR spectra of the dehydrochlorinated PVC with PEG 400: DPVC-C (24 h, with stirring) and DPVC-D (15 min, with stirring).

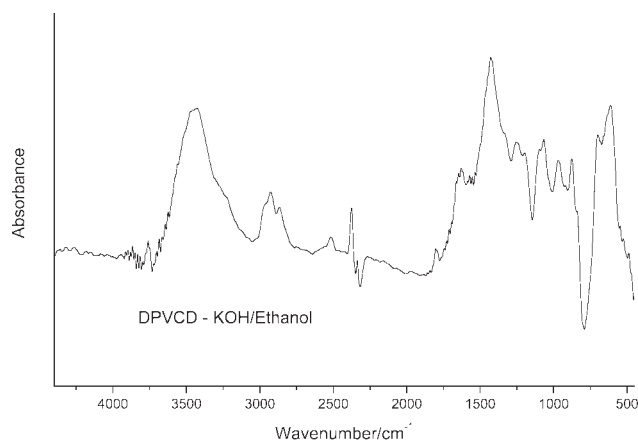


Figure 4 FTIR spectrum of DPVC-E (KOH/ethanol).

in relation to DPVC-A was that the oxidation side reactions occurred to a lesser extent.

Chemical modification during film formation is an interesting way to produce rechargeable batteries from the dehydrochlorination process with the electrochemical activity of the product due to polyene structure formation.¹¹ In the use of dehydrochlorinated samples as intermediate, the process can be modified to avoid film formation and to improve the superficial area for the reaction. In this case, the dehydrochlorinated procedure was performed in a closed recipient to prevent fast evaporation of the solvent. After 24 h, the organic phase showed a red to brown color because of the dehydrochlorination of PVC dissolved in a viscous THF solution (DPVC-C sample). A similar aspect was observed for the sample treated for 15 min (DPVC-D). The solution color was less intense than for the sample dehydrochlorinated for 24 h, which indicated a partial dehydrochlorination of this material.

Figure 3 shows the FTIR spectra of DPVC-C and DPVC-D. The main absorption bands observed for DPVC-C [Fig. 3(a)] were at 3400, 1720, 1640, 1560, and 1010 cm^{-1} . The presence of these bands confirmed the formation of a heterogeneous material formed by the elimination and nucleophilic products on the polymeric chain. The absorption bands at 1564 and 1010 cm^{-1} were intense, which indicated a high conversion of the dehydrochlorination process. Another important aspect was the modification of the frequency position, which was an indication of a long set of conjugations because the band assigned to C=C stretching in a conjugated system tends to appear at lower frequencies, whereas the opposite behavior is expected for the band assigned to =C-H, which tends to shift to higher frequencies.¹¹

The pattern of the FTIR spectra of DPVC-D was similar to that seen in the DPVC-C sample except for the region from 2000 to 1500 cm^{-1} . For DPVC-D,

there was a peak of medium intensity in this region, which was different from that previously seen for DPVC-C. The process of dehydrochlorination was confirmed by the presence of the FTIR bands at 1634 and 1105 cm^{-1} . This process provided an intermediate reaction conversion compared to that of DPVC-C; the decrease in dehydrochlorination conversion could be verified by the small contribution or absence of bands at 1564 and 1010 cm^{-1} . An important aspect was the absence of the band assigned to C=O bond stretching, which indicated low oxidation of the sample.

Potassium hydroxide is a strong nucleophile that has limited solubility in organic solvents. The use of PEG as a catalyst allows the elimination reaction, although there are concomitant side reactions, such as nucleophilic substitution and oxidation. With the aim of evaluating the dehydrochlorination process without PEG, we solubilized the nucleophile in ethanol. Despite ethanol being a protic solvent, its dielectric constant is lower than water, and it should have improved the interaction between the PVC/THF phase and the KOH/ethanol system. The FTIR spectrum for the dehydrochlorinated material (DPVC-E) is shown in Figure 4.

DPVC-E showed a yellow brownish color with 24 h of reaction time. Elimination was evidenced by the presence of bands at 1628 and 970 cm^{-1} . However, the FTIR spectrum for this sample showed low resolution, and some peaks were not well resolved, which created some wide bands with low definition. This aspect was different from that observed for the FTIR spectra of the samples dehydrochlorinated with PEG.

The presence of the band assigned to O-H stretching indicated a possible nucleophilic substitution. This could be emphasized by the presence of the band at 1066 cm^{-1} attributed to C-O deformation.

TABLE II
Main FTIR Absorption Assignments for the Chemically Modified PVC Samples

| Wave number (cm^{-1}) | Assignment |
|----------------------------------|--|
| Dehydrochlorination process | |
| 3500–3400 | O–H stretching (substitution reaction) |
| 1760–1700 | C=O stretching (oxidation) |
| 1620–1540 | C=C stretching (formation of polyenic structure—elimination reaction) |
| 1010–950 | =C–H out of plane deformation (formation of polyenic structure—elimination reaction) |
| Sulfuric acid treatment | |
| ~ 1190 | O=S=O asymmetric stretching |
| ~ 1020 | O=S=O symmetric stretching |
| ~ 880 | S–OH symmetric stretching |

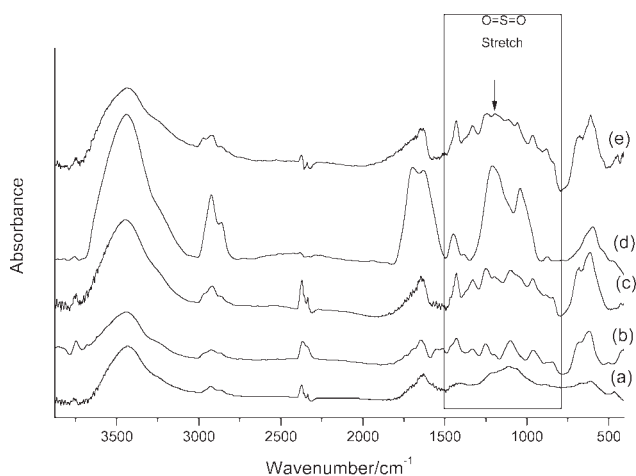


Figure 5 FTIR spectra of the sulfonated DPVC: (a) SDPVC-A, (b) SDPVC-B, (c) SDPVC-C, (d) SDPVC-D, and (e) SDPVC-E.

Sulfonation

Low-molecular alkenes reacted with sulfuric acid to form alkyl hydrogen sulfates. For dehydrochlorinated PVC, this reaction can be more complicated. As was observed in the previous discussion, the dehydrochlorinated samples presented double bonds, which depending on the process, presented long sequences of conjugations, as observed for DPVC-C. Yet, some DPVC FTIR spectra showed the presence of hydroxide, chlorine, and carbonyl groups. The polyene underwent electrophilic addition, which allowed the formation of sulfonated PVC derivatives. DPVC samples reacted with concentrated sulfuric acid, and the FTIR spectra of the produced samples are shown in Figure 5 and 6.

The sulfonation process can be evaluated through the presence of peaks in the region between 1200 and 1000 cm^{-1} . The main bands observed for the SDPVC samples are summarized in Table II. In Figure 5(a), the broad shape peaks in region between 1200 and 1000 cm^{-1} of the spectrum suggest the presence of bands assigned to O=S=O stretching.⁷ In this region for SDPVC-A, the bands at 1030 cm^{-1} and 1180 cm^{-1} were present in a broad shape band, which was difficult to separate, but the presence of these bands was evidence of the presence of the O=S=O groups in the PVC modified structure. Also, the presence of the band at 1630 cm^{-1} was indicative of double bonds in the polymer structure, which could have been reminiscent of the dehydrochlorination process or formed during sulfuric acid treatment.

For the SDPVC-B sample, the sulfonation seemed to be ineffective. The broad band observed in the region from 1200 to 1000 cm^{-1} for SDPVC-A [Fig. 5(a)] was not present. Its FTIR spectrum [Fig. 5(b)]

showed an intensity increase for the band at 1644 cm^{-1} and the rising of a band at 1514 cm^{-1} . The presence of the band at 1514 cm^{-1} was attributed to double-bond formation in a medium or long conjugated system. This band did not appear in the FTIR spectrum for the dehydrochlorinated sample DPVC-B, which indicated the formation of new double bonds after the sulfuric acid treatment. The SDPVC-C spectrum [Fig. 5(c)] presented almost the same bands observed for SDPVC-B with the exception of a medium-intensity band at 1178 cm^{-1} , which appeared in this sample and was assigned to O=S=O asymmetric stretching. In this case, low sulfonation of DPVC-C was observed.

The sample dehydrochlorinated for 15 min after treatment with sulfuric acid (SDPVC-D) showed, in the FTIR spectra, an intense band at 1695 cm^{-1} attributed to C=O stretching, which indicated the formation of a product with carbonyl groups. In the region between 2000 and 1100 cm^{-1} , there was an intense band that could be separated into two peaks due to the presence of a shoulder at 1190 cm^{-1} [Fig. 6(d)]. The presence of this shoulder was assigned to the material sulfonation.

The SDPVC-E FTIR spectrum showed a broad set of bands from 1280 to 1080 cm^{-1} with emphasis on a strong band at 1186 cm^{-1} , which evidenced the sulfonation of the polymer.

Important information about the spectra in Figure 5(a-c,e) was the presence of bands at 3440 and about 1640 cm^{-1} , which indicated the presence of hydroxyl groups and double bonds, respectively. The band at 1640 cm^{-1} was broad for all of the samples; this was probably because of a low contribution of carbonyl groups related to oxidation during the reaction.

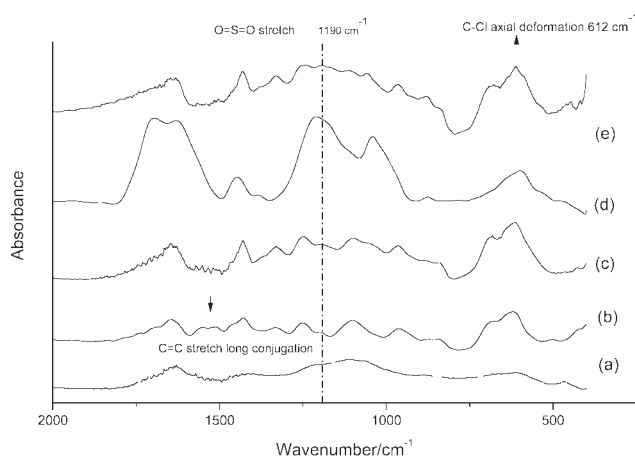


Figure 6 FTIR spectra of the sulfonated DPVC in the region between 2000 and 400 cm^{-1} : (a) SDPVC-A, (b) SDPVC-B, (c) SDPVC-C, (d) SDPVC-D, and (e) SDPVC-E.

Mechanism of sulfonation

PVC sulfonation was more effective in the sample with higher chlorine elimination, which led to higher double-bond formation, that is, DPVC-A [Fig. 6(a)] and DPVC-D. Although DPVC-D presented an intermediated degree of dehydrochlorination, sulfonation and oxidation occurred, which led to the formation of heterogeneous products with sulfonated and carbonyl groups. Although sulfonation occurred, the intensity of the band related to C=C stretching was maintained. This may have been evidence of a competitive process of sulfonation and the new polyenization of the PVC. This process seemed to be dependent on the presence of other functional groups, such as hydroxyl or chlorine, that remained in the polymer structure. The explanation for the difference of reactivity for the dehydrochlorinated samples in relation to sulfonation is associated with the conversion of the elimination and nucleophilic addition reactions.

Indications for this proposal appear in the literature for other vinyl polymers, such as polyenized poly(vinyl alcohol), which may produce fibers with cation-exchange capacities. The sulfonic ester groups were introduced by a sulfonation reaction with hydroxyl groups of the remaining vinyl alcohol units.⁴ This possibility was similar to the process observed in this study.

CONCLUSIONS

A mixture of sulfonated and polyenized PVC polymer was produced from sulfonation of dehydrochlorinated waste PVC pipes. FTIR spectra showed

that the dehydrochlorinated samples were heterogeneous materials that showed different proportions of elimination products, hydroxyl substitution, and partial oxidation, depending on the dehydrochlorination route. This proportion of products in polymeric chain led to the formation of polymers with different sulfonation conversions, as was confirmed through the highest sulfonation conversion observed for DPVC-A and DPVC-D.

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