Journal of the University of Chemical Technology and Metallurgy, 44, 3, 2009, 253-256

FEEDSTOCK RECYCLING OF POLY(VINYL CHLORIDE-CO-VINYL ACETATE): ALKALINE DECHLORINATION IN ORGANIC SOLVENTS

J. Blazevska-Gilev, D. Spaseska

Faculty of Technology and Metallurgy,
St.Cyril and Methodious University, P.O. Box 580,
MK-1001 Skopje, Republic of Macedonia
E-mail: jadranka@tmf.ukim.edu.mk

Received 16 April 2009
Accepted 12 May 2009

ABSTRACT

Mild alkaline hydrolysis of poly(vinyl chloride-co-vinyl acetate) (P(VC/VAc)) in an organic solvent, accompanied with an acceptable level of dechlorination, was the present study of chemical recycling of poly(vinyl chloride-co-vinyl acetate). In the itinerary of hydrolysis with NaOH under atmospheric pressure dimethylsulfoxide was put in at 30-80 °C for 1-4 hours. The resulting hydrolysis product is poly(vinyl alcohol) with slightly chlorine content. The only one by-product was sodium chloride and no other harmful products were produced.

The process design for this procedure has been derived on the base of the experimental planning method resulting in a derived mathematical model for the degradation processes by varying the main process parameters: solvent concentration, hold-up time and temperature. The reflection function was the concentrations of the chlorine ions. The intensity of the degradation process is dependent mainly on the DMSO concentration.

Keywords: *poly(vinyl chloride-co-vinyl acetate), P(VC/VAc) recycling, plasticizer separation, dechlorination in organic solvents.*

INTRODUCTION

The reuse of wastes is important from different point of view. Wastes and industrial by-products should be considered as potentially valuable resources merely awaiting treatment and application [1]. Recycling of plastic waste have several advantages: conservation of non-renewable fossil fuels – plastic production uses 8 % of the world's oil production, 4 % as feedstock and 4 % during manufacture; reduced consumption of energy; reduces amounts of solid waste going to landfill; and reduced emissions of carbon dioxide (CO_2), nitrogen oxide (NO) and sulphur dioxide (SO_2) [2]. Recycling techniques, such as reprocessing with virgin resin, blending and pyrolysis of waste plastics, recycling through solutions and chemical reactions, are effective routes to reduce the plastic wastes [3]. Recycling of plastic waste is difficult owning to contamination by plasticizer and stabilizers in the commercial plastic material. Phtalic esters, phosphoric esters and ethylene glycol are widely used as plasticizers, among which, the phtalic ester is the most popular [4]. For better separation of the plasticizer, a treatment using alkali solution, a stable chemical, was proposed by Sin at al. [5].

In this study a mild procedure for treating waste P(VC/VAc), which involves dechlorination by an alkaline medium has been investigated.

EXPERIMENTAL

A soft foil of poly(vinyl chloride-co-vinyl acetate), commercially available from OHIS Factory of Skopje, was used as an investigating material.

A 0.0100 mol/l NaCl standard solution and 0.010 mol/l $AgNO_3$ to be standardized for determination the chlorine concentration were prepared. A 0.2 % fluorescein sodium ($C_{20}H_{10}O_5Na_2$) solution was prepared as an indicator for chloride ion titration (for Fajans method) using 0.20 g fluorescein sodium and 100 g water. Fajans method is used in the range of pH 7-10. The examined P(VC/VAc) with aqueous solution of NaOH were placed in a 300-ml three-necked flask equipped with a stirrer, heated at the temperature between 30-80°C, for 1-4 hours. After the reaction was complete, it was cooled and precipitates were collected by filtration. The product being washed with water and dried became brown.

The reaction of P(VC/VAc) with NaOH produces a partially cross-linked polyvinyl alcohol (Fig. 1), which precipitates are insoluble in any one of the solvents like dimethylsulfoxide (DMSO), pyridine, etc. The general procedure for dechlorination was as follows. To a solution of P(VC/VAc) in an organic solvent (DMSO) aq.NaOH was added and the resulting mixture was heated with stirring under an atmospheric pressure. Dechlorination of P(VC/VAc) in DMSO (40-50ml) was conducted in a homogeneous system at the temperature from 30-80°C for 1-4 hours. The mixture was stirred at the stirring rate of 300 rpm continuously during the reaction.

RESULTS AND DISCUSSION

The alkaline dechlorination of poly(vinyl chloride-co-vinyl acetate) in dimethylsulfoxide (DMSO) is significant, because of carrying it out at low temperature. The resulting hydrolysis product is poly(vinyl alcohol) with a controlled chlorine content (Fig. 1).

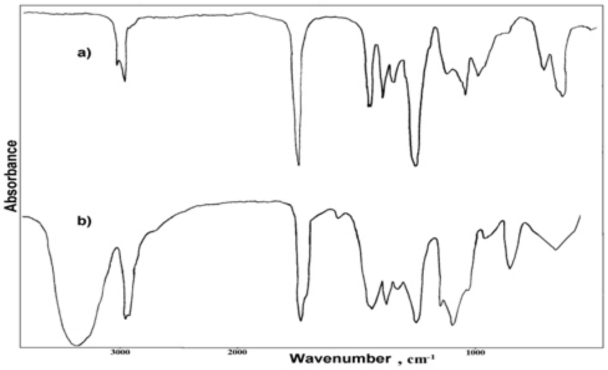


Fig. 1. (a) Initial poly(vinyl chloride-co-vinyl acetate); (b) obtained poly(vinyl alcohol).

The spectral pattern of initial P(VC/VAc) (Fig. 1a) consists [6,7] of absorption bands at 2970, 2910 and 2843 cm^{-1} (-C-H stretches), 1736 cm^{-1} (C=O stretch), 1424 and 1439 cm^{-1}, 1424 cm^{-1} (CH_3 rocking), 1372, 1330, 1237, 1100, and 1024 cm^{-1} (C-O stretch coupled with C-C vibrations), 966 cm^{-1} (skeletal vibrations) and 740, 635 and 612 cm^{-1} (C-Cl stretches and skeletal vibrations) [8,9]. The IR spectrum of hydrolysed P(VC/VAc) (Fig. 1b) showed a broad absorption band around 3400 cm^{-1}, pointing out the existence of the hydroxyl group as for poly(vinyl alcohol). New absorption band was found around 1600 cm^{-1}, which corresponds to the C=C double bond structure.

The analysis of poly(vinyl alcohol) was conducted by IR spectroscopy for the purpose of determining the (C-Cl/C-H) ratio of the degraded and virgin polymer.

The (C-Cl)/(C-H) ratio of the degraded polymers is half of the initial value of the starting polymers. The relative absorptivity of the n(C-Cl) bands and n(C-H) bands of the initial P(VC/VAc) and the end-obtained polymer are given in Table 1.

Taking into account the obtained results for the copolymer, consequently compared by the relative apsorptivity of the ν(C-Cl) bands and ν(C-H) bands for PVC [10], a controlled degradation (mainly greater than in the case of the homopolymer, PVC) was observed.

Table 1. The relative absorptivity of the ν(C-Cl) bands at 820-615 cm^{-1}, and ν(C-H) bands at 3100-2800 cm^{-1} of the virgin and the obtained polymer.

relative absorptivity	P(VC/VAc) virgin	P(VC/VAc) degraded
ν(C-Cl)	5.3985	11.771
ν(C-H)	5.2551	25.792
ν(C-Cl/C-H)	1.0273	0.4564

Table 2. The evolved Cl as NaCl in dependence on the experimental conditions for poly(vinyl chloride-co-vinyl acetate) hydrolysis.

No	x_1 ml DMSO	x_2 Time / hours	x_3 T / °C	y $c \cdot 10^{-3}$, mol dm^{-3} NaCl
1	40	1	30	0,2320
2	50	1	30	0,3320
3	40	4	30	0,2980
4	50	4	30	0,3650
5	40	1	80	0,6964
6	50	1	80	0,8291
7	40	4	80	0,7627
8	50	4	80	0,8954

The degradation is appeared as a result of the realised acids from the both monomers of copolymer. McNeill I.C has released that each acid evolved from the copolymer catalyzes side group elimination in the other co-monomer [11]. That means that when once a double bond has been formed, the neighboring chain units are destabilized towards acid loss.

For the purpose of the determination the dependence of the concentration of Cl ions on the content of DMSO, hold-up time and temperature, the experiments have been carried out in accordance with the experimental planning method resulting in a derived mathematical model for the mentioned degradation process [12]. As the reflection functions, the concentrations of the chlorine ions have been taken. The obtained results are presented in Table 2.

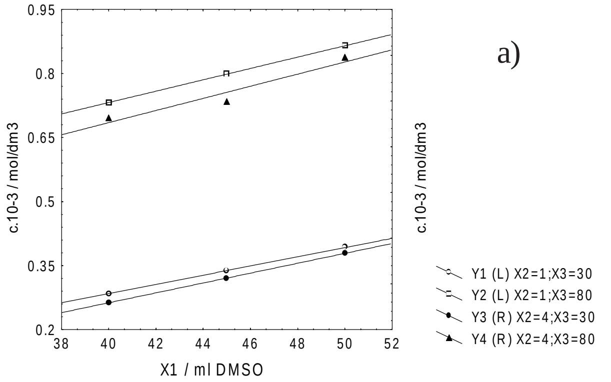
The derived equation with coded variables for the concentration of the Cl ions is given with the relationship:

$$Yx = 0{,}5513 + 0{,}054X_1 + 0{,}2445X_3 \qquad (1)$$

The equation with natural variables is given by the following relationship:

$$y(x) = -0{,}4726 + 0{,}0108x_1 + 0{,}0098x_3 \qquad (2)$$

The dependences of the concentration of the released Cl ions on the content of DMSO (x_1), and temperature (x_3), are presented in Fig. 2 (a and b).



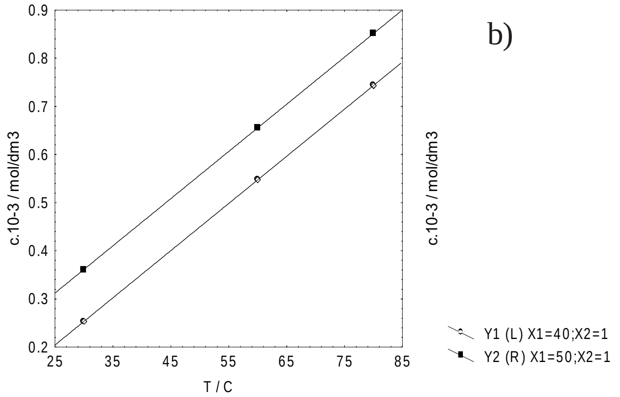


Fig. 2. Dependence of the concentration of the Cl ions: (a) on the ml of DMSO (x_1) and (b) on the temperature (x_3) of the treated copolymer.

According to the relationship (1) it is possible to conclude that the both relevant parameters of the investigated process (DMSO content ant temperature) have positive effect to the concentration of Cl ions. The most expressed influence on the reflection function has the parameter temperature of treatment.

CONCLUSIONS

- The used alkaline dechlorination of poly(vinyl chloride-co-vinyl acetate) in organic solvents process demonstrated high percent of dechlorination from P(VC/VAc) under comparatively mild conditions using NaOH in DMSO at different temperature for 1-4 hours and atmospheric pressure.
- The resulting main product of P(VC/VAc) treatment in organic solvent (dimethylsulfoxide) is poly (vinyl alcohol) with controlled chlorine content (Table 2).
- Hydrochloric and acetic acids are appeared as the evolved products of the hydrolytic process of P(VC/VAc), which elimination results in progressive decrease in stability of the copolymer [11].
- The evolved chlorine content in the course of the degradation process is positively dependent, mainly on the temperature of treatment followed by the content of DMSO.
- The low temperature treatment is an advantage for the recycling processes because the only one by-product was formed, sodium chloride and no other harmful products were produced.
- The experimental planning method was a successfully used method for the process carrying out under the controlled conditions, as well as for obtaining a recycled new polymer with a controlled content of chlorine.

REFERENCES

1. Zainab Z. Ismail, Enas A.Al-Hashmi, Waste Management, **28**, 2008, 2041-2047.
2. Rafat Siddique, Jamal Khatib, Inderpreet Kaur, **28,** 2008, 1835-1852.
3. Ayman M.Atta, Manar E.Abdel-Raouf, Shimaa M.Elsaeed, Abdel-Azim A., Progress in Organic Coatings, **55,** 2006, 50-59.
4. Shun Myung Shin, Ho Seok Jeon, Young Han Kim, T Yosioka, A Okuwaki, Polymer Degradation and Stability, **78,** 2002, 511-517.
5. S. M.Shin, T.Yoshioka, A.Okuwaki, Polym. Degrad. Stab., **61**, 1998, 349-353.
6. Dolphin D., Wick A., Tabulatuion of infrared spectral data. Wiley, New York, 1977.
7. Miller RGJ., Willis HA., editors. Infrared structural correlation tables data cards.
8. N.Bensemra, TV. Hoang, A.Michel, M.Bartholin, A.Guyot, Polym. Degrad. Stab., **23**,1989, 35.
9. N. Bensemra, TV. Hoang, A. Guyot, M. Gay, L.Carette, Polym. Degrad. Stab., **24,**1989, 89.
10. J. Blazevska-Gilev, D. Spaseska, J. Univ. Chem. Technol. Met. (Sofia), **42**, 1, 2007, 29-34.
11. I.C. McNeill, J. Anal. Appl. Pyrol., **40**, 1997, 21.
12. S.N. Sautin, Plan. Exp. Chem & Chem. Technol., Leningrad, **7**, 1973, (in Russian).