

Converting Waste Plastic Containing Acrylonitrile into a Water-Absorbent Polymer

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ABSTRACT: Waste ABS (acrylonitrile-butadiene-styrene) resin and waste AS (acrylonitrile-styrene) resin used for video cassettes were converted into a water-absorbent polymer. Concretely, these waste resins containing acrylonitrile were made to react with heated high-concentration sulfuric acid. In this chemical modification, the acrylonitrile portion and the styrene portion in the AS resin were hydrolyzed and sulfonated, respectively. We studied the relationship between the water absorbency of the modified waste AS and the con-

ditions of chemical modification. It was confirmed that the water absorbency greatly depends on the degree of hydrolysis of the acrylonitrile portion in the waste AS resin. We have succeeded in developing a water-absorbent polymer, which can absorb water of about 800 times of its own weight by the chemical modification of the waste AS resin. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 689–693, 2008

Key words: waste; plastics; recycling; swelling; modification

INTRODUCTION

There are various methods of recycling waste plastic, such as material recycling, chemical recycling, and energy recovery,^{1–9} but most methods of recycling waste plastic produce less functional material. We have developed a new technology to convert waste plastic into value-added materials such as polyelectrolyte. In our past research, we reported a new technology to convert waste polystyrene used as cushions and cases for electrical appliances into a polymer flocculent for wastewater treatment, as shown in the upper part of Figure 1.^{10–12}

We focused our attention on ABS resin and AS resin, which are the most used for household electrical appliances after polystyrene.^{13,14} We have succeeded in converting waste ABS resin and waste AS resin used for professional video cassettes into a water-absorbent polymer by causing these resins to react with heated high-concentration sulfuric acid. See the lower part of Figure 1. It is considered that the acrylonitrile portion in the resin is hydrolyzed and the styrene portion in the resin is sulfonated in this chemical modification. We focus here on the relationship between the water absorbency of mainly the modified waste AS resin and the conditions of chemical modification, because the chemical structure of AS resin is simpler than that of the ABS resin.

EXPERIMENTAL SECTION

Chemical modification of waste resin

The shells and reels of used professional video cassettes were used as waste ABS resin and waste AS resin, respectively. For comparison, waste PS (polystyrene) from the transparent case for used CDs, waste HIPS (high-impact polystyrene) from used VHS cassette shells, a reagent-grade AS resin, and commercial-grade AS resins containing various amounts of acrylonitrile were used as raw materials. The molecular weight of the resins was measured using GPC (gel permeation chromatography) in an Ultra Styragel Plus MX (N22115) column from Waters Ltd. with chloroform as the mobile phase. The acrylonitrile content in the resins was determined by FTIR (Fourier transformation infrared spectrum) measurement. The waste resins were first crushed into powder of a 16–32 mesh with a labo-crusher while cooling with liquid nitrogen. Five grams of the powder was then made to react with 250 g of a heated high-concentration sulfuric acid. As the reaction advanced, the resin powder gradually swelled to generate the gel. After the reaction was over, the swelled-up gel was filtered using a glass filter and repeatedly washed with pure water until the pH was 5. Then the swelled-up gel was dried in an oven at 105°C for 2 h to remove moisture. The FTIR (Fourier transform infrared) spectrum of the dried gel was measured with a Nicolet Avatar 360. The sulfur content in the dried gel was determined using the combustion flask method.¹⁵

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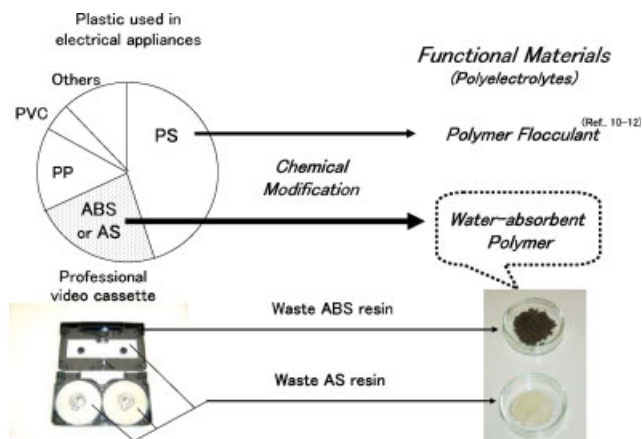


Figure 1 Converting waste plastic into functional materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Measurement of the water absorbency of the modified resin¹⁶

Pure water (200 g) was added to 0.1 g of the modified resin (A) in a 300-cm³ glass beaker, and the resin was allowed to swell sufficiently for 30 min. The swollen resin was filtered through a 60-mesh screen for 30 min, and the remaining swollen resin was weighted (B). The water absorbency was calculated by the following equation:

$$\text{Water absorbency of the modified resin (g of water/g of dry resin)} = (B - A)/A.$$

RESULTS AND DISCUSSION

Table I shows the water absorbency of the various modified resins. When AS and ABS resins containing acrylonitrile were used as raw materials, they were sulfonated and the resulting modified resins had

water absorbency. However, when waste PS and HIPS not containing acrylonitrile were used as raw materials, the resulting modified resins were essentially not sulfonated and could not absorb water. These results indicate that the water absorbency of the modified resins depends on the amount of acrylonitrile in the original resin.

The FTIR spectra of waste AS resin from the used provideo reels and the resulting modified waste AS resin are shown in Figure 2. The waste AS resin was reacted with sulfuric acid of a 90 wt % at 100°C for 30 min. The cyano group of acrylonitrile in the waste AS resin was hydrolyzed to convert into a carboxyl group of 1720 cm⁻¹ (Ref. 17) and an amide group of 1650 cm⁻¹.¹⁷ As a result, no absorption of the cyano group was found in the modified AS resin. It was also confirmed that the benzene ring in the styrene group was sulfonated to introduce a sulfonic acid group of 1034–1145 cm⁻¹.^{18–20}

Figure 3 shows the reaction formula of the chemical modification of the waste AS resin using heated high-concentration sulfuric acid. The cyano group of acrylonitrile in the waste AS resin is converted into amide groups and carboxyl groups by hydrolysis, and a sulfuric acid group is introduced into the benzene ring in styrene by sulfonation. That is, the waste AS resin is simultaneously hydrolyzed and sulfonated by the reaction with heated high-concentration sulfuric acid. It seems clear that the hydrolysis and sulfonation contribute to the water absorbency of the modified waste AS resin. We studied the relationship between the water absorbency of the modified waste AS resin and the conditions of chemical modification. The results are shown in Figs. 4–8 and Table II.

Figure 4 shows the relationship between the water absorbency and sulfur content of the modified resin obtained when waste AS resin reacts with sulfuric acid of a 97 wt % at various temperatures for

TABLE I
Details of the Chemical Modification of Various Resins

Resin	Raw materials			Resulting resins ^a	
	Roots	Acrylonitrile contents ^b (wt %)	M_w^c	Sulfur contents ^d (wt %)	Water absorbency ^e (g/g)
AS	Provideo reels	29	117,000	12.7	48.2
AS	Reagent grade	25	173,000	13.8	39.7
ABS	Provideo cassette shells	26	–	10	26.7
PS	Transparent cases	–	310,000	0.02	1.76
HPS	VHS video cassette shells	–	220,000	0.81	1.53

^a Chemical modification: resin/H₂SO₄ (97 wt %) = 1/50 (wt %/wt %), 80°C × 30 min.

^b Determined by FTIR spectrum.

^c Determined by gel permeation chromatography (GPC) in chloroform.

^d Measured using the combustion flask method.

^e Absorbency = g dry resin/g swollen resin. Each resin filtrated by 60 mesh.

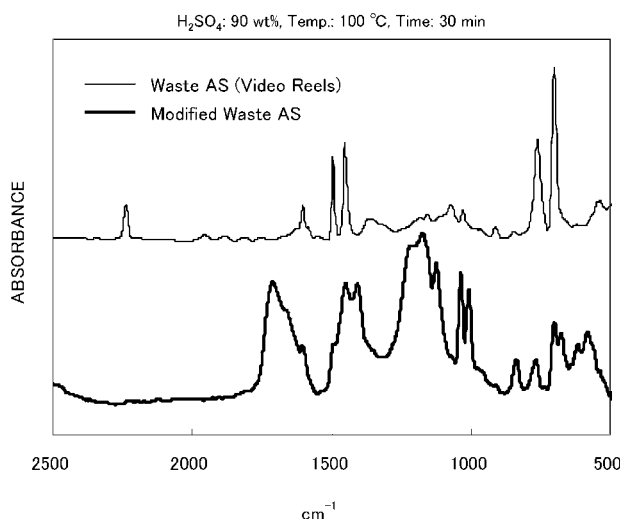


Figure 2 FTIR spectra of waste AS resin and the modified waste AS resin.

30 min. The sulfur content in the modified AS resins increases with the rise of reaction temperature, and their water absorbency increases rapidly above 80°C.

Figure 5 shows the FTIR spectra of the modified AS resins shown in Figure 4. No CN stretching peak of acrylonitrile at 2247 cm⁻¹ was seen in the modified waste AS resins obtained when the waste AS resin was reacted at 80°C. This indicates that the original waste AS resin was completely hydrolyzed to convert the cyano groups into amide groups or carboxyl groups under the high temperature after the chemical modification.

Figure 6 shows the relationship between the water absorbency and sulfur content of the modified waste AS resins obtained when the waste AS resins react with sulfuric acid of different concentrations at 100°C for 30 min. We could obtain a water-absorbent polymer, which has the ability to absorb the water about 800 times of its own weight using sulfuric acid of a 90 wt %. In this case, the sulfur content in the modified waste AS resin gradually increases as

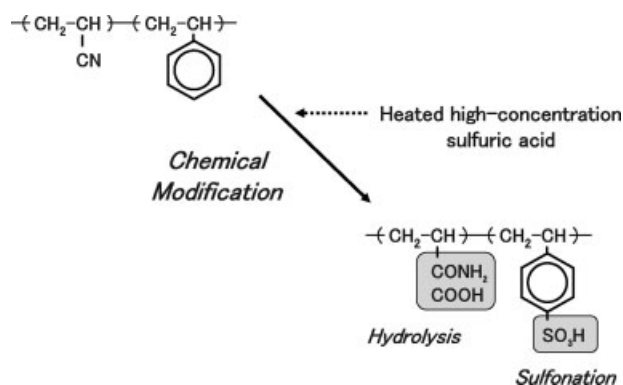


Figure 3 Chemical modification of waste AS resin.

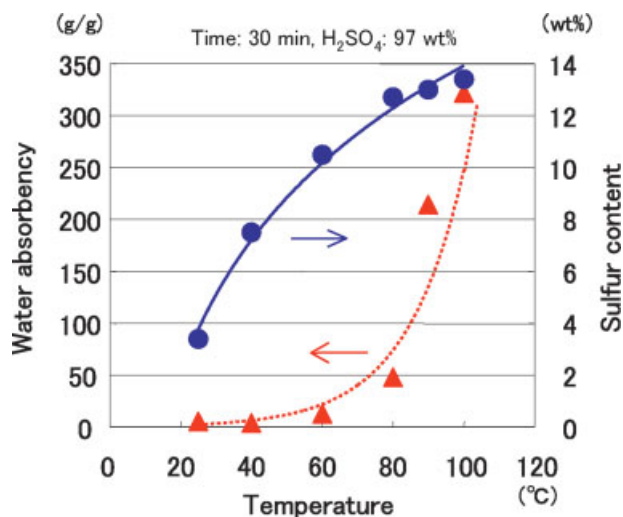


Figure 4 The effect of reaction temperature on the water absorbency and sulfur content of the modified waste AS resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the concentration of sulfuric acid increases. On the other hand, as regards water absorbency, the sulfur content gradually decreases. This figure may indicate that the water absorbency of the modified waste AS resins depends not on the degree of sulfonation of styrene but on the hydrolysis of acrylonitrile in the waste AS resin. These results show a tendency similar to the results reported by Lim et al.,²¹ although the chemical structure and the hydrolysis method are different from those of our water-absorbent polymer and our hydrolysis method.

To confirm this hypothesis, the FTIR spectra of the modified AS resins shown in Figure 6 are shown in Figure 7. As there is no CN stretching peak of acrylonitrile at 2247 cm⁻¹ in the either modified AS resin, the cyano group in the waste AS resin must

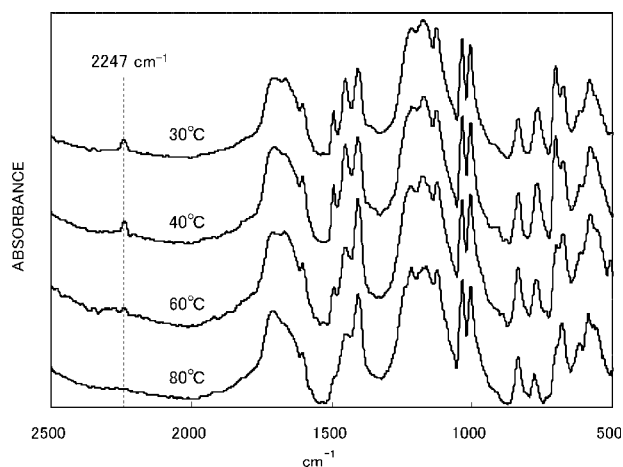


Figure 5 FTIR spectra of the modified waste AS resins under various temperatures.

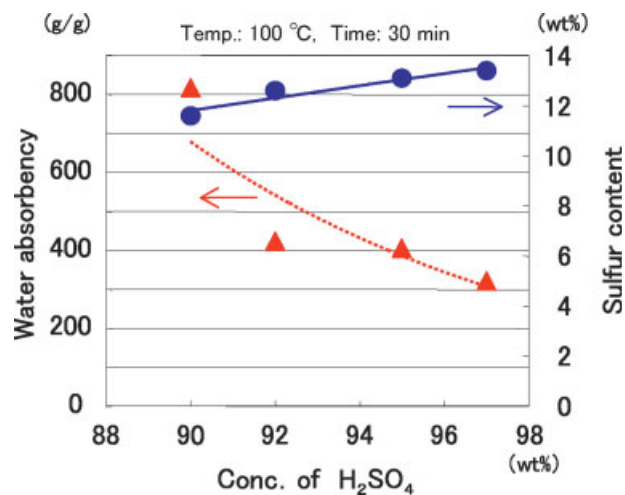


Figure 6 The effect of the concentration of sulfuric acid on the water absorbency and sulfur content of the modified waste AS resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

have been completely converted into an amide group or a carboxyl group. Also, the difference in the peak heights of the carboxyl group of 1720 cm^{-1} and the amide group of 1650 cm^{-1} of the modified AS resin reacted with sulfuric acid of 90 wt % is more remarkable than that of the modified waste AS resin reacted with sulfuric acid of 97 wt %. Concretely, the peak of the carboxyl group is much higher than the peak of the amide group when the waste AS resin reacted with sulfuric acid of 90 wt %. This indicates that the amide group is converted into a carboxyl group as the hydrolysis of the cyano group in the waste AS resin progresses.

Figure 8 shows the relationship between the water absorbency of the modified AS resins and the content of acrylonitrile in the original AS resins. The details of the various AS resins used as a raw mate-

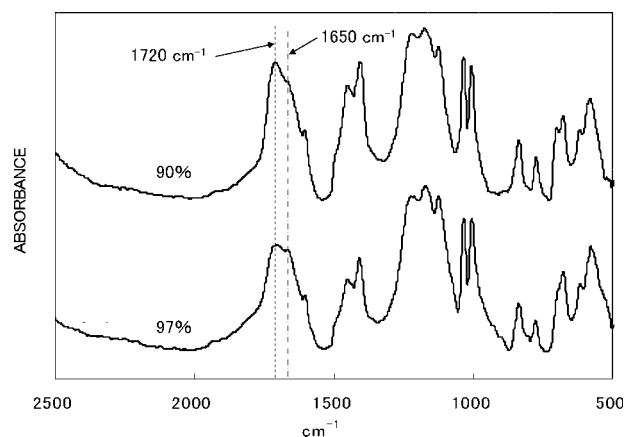


Figure 7 FTIR spectra of the modified waste AS resins under different concentrations of sulfuric acid.

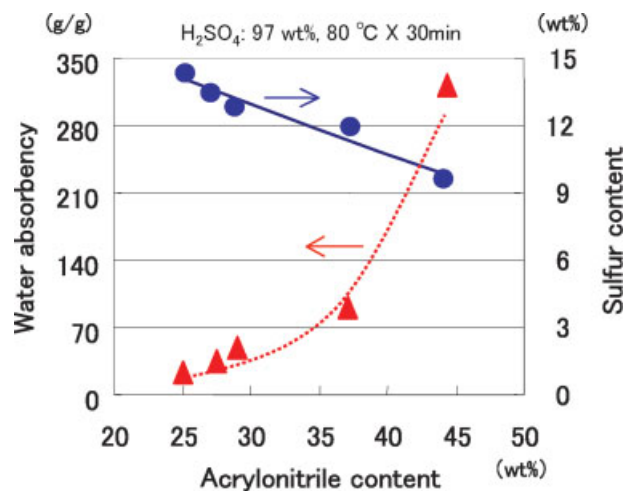


Figure 8 The effect of the acrylonitrile content on the water absorbency and sulfur content of the modified AS resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rial for the chemical modification are shown in Table II. Each AS resin was reacted with sulfuric acid of a 97 wt % at 80°C for 30 min. The water absorbency of the modified AS resins increases as the acrylonitrile content in the AS resin increases, showing that the water absorbency of the modified resins depends on the degree of hydrolysis of acrylonitrile in the AS resin. It is considered that the amide group and the carboxyl group generated by the hydrolysis of acrylonitrile greatly influence the water absorbency of the modified resins. This means that we can synthesize good water-absorbent polymers and good ion-exchange resins by controlling the hydrolysis of the cyano group and the sulfonation of the benzene ring in the AS resin.

Figure 9 shows the modified waste AS resin before and after absorbing water. The surface of the modified AS resin before water absorption has many small holes of $1\text{ }\mu\text{m}$ or less in diameter. After water absorption, the diameter of the small holes increases to several microns with the swelling.

TABLE II
The Various AS Resins Used as a Raw Material for the Chemical Modification

Raw material	Molecular weight			Monomer content (wt %)	
	M_w	M_n	d	Styrene	Acrylonitrile
Commercial grade 1	128,600	63,060	2.04	72.5	27.5
Commercial grade 2	116,500	54,830	2.12	62.9	37.1
Commercial grade 3	81,700	43,920	1.86	55.6	44.4
Provideo reels	117,400	54,260	2.16	71	29
Reagent grade	173,300	79,360	2.18	75	25

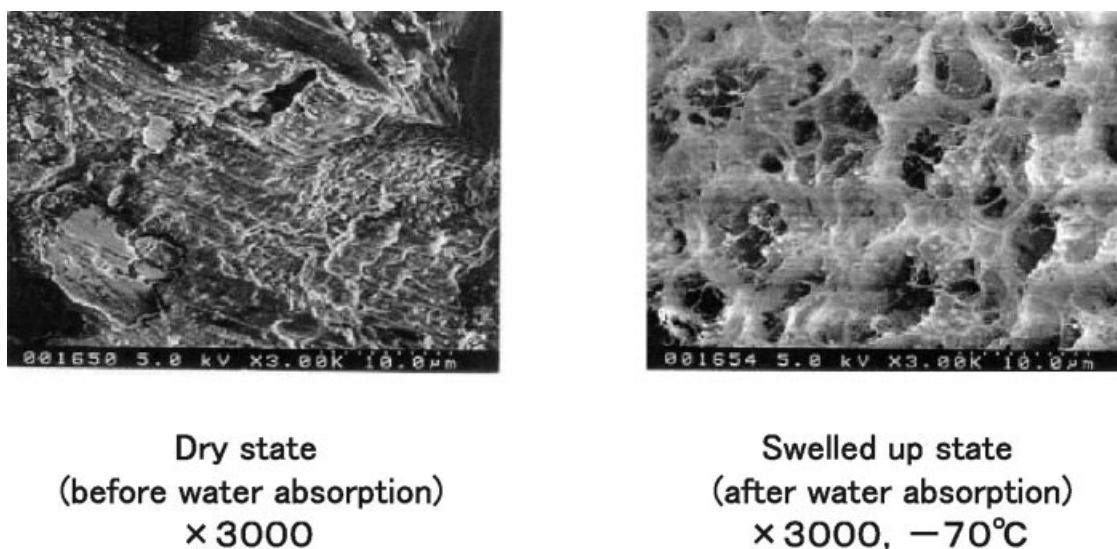


Figure 9 The modified waste AS resin.

CONCLUSIONS

1. Waste resin containing acrylonitrile can be converted into a water-absorbent polymer to absorb water of about 800 times of its own weight by reacting with heated high-concentration sulfuric acid.
2. The styrene and acrylonitrile in the waste AS resin were sulfonated and hydrolyzed, respectively, to generate an amide group and a carboxyl group by the chemical modification.
3. Resins without acrylonitrile such as polystyrene and high-impact polystyrene were essentially not sulfonated under the same reaction conditions. In other words, the hydrolysis of acrylonitrile in the resins contributes to the sulfonation of styrene in the resin.
4. The degree of water absorbency of the modified waste AS resin is greatly influenced by the hydrolysis of acrylonitrile in the resin. The water absorbency of the modified waste AS resin increases as the acrylonitrile contents in the resin and the reaction temperature increase, and as the concentration of sulfuric acid decreases.
5. Various water-absorbent polymers with different degrees of water absorbency can be produced by controlling the degree of hydrolysis of acrylonitrile in the resin.

We hope that this study contributes to converting waste plastic containing acrylonitrile such as AS and ABS resin into functional materials such as water-absorbent polymers and ion-exchange polymers.

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