Supercritical Water Cracking and Washing of Used Polymer

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A rubber polymer (EPDM, ethylene-propylene-diene-terpolymer) and its vulcanized rubber were cracked to paraffin oil (PO) in NaOH-containing supercritical water (SCW) at 420 °C and 30 MPa. PO recovered as a hexane-soluble cracking component could be recycled as the rubber softener because sulfurs added to the rubber for the elasticity were washed out in SCW. The SCW polymer cracking is not oxidative but reductive. The ^{13}C -NMR analysis of PO obtained by SCW D_2O cracking demonstrates that the terminal methyl carbons are deuterated as a clear indication of hydrogen supply by SCW. [supercritical water, rubber, cracking, recycle, reductive]

1. Introduction

SCW, water at $> 374\text{ }^\circ\text{C}$ and $> 22.1\text{ MPa}$, can be an attractive reaction field with a high kinetic energy by enabling us to attain a new reaction pathway which is not available in ambient water due to a high energy barrier, a low reactant solubility or a low molecular diffusivity [1-4]. Solubility or mixing of "hydrophobic" substances is markedly increased in SCW without a surfactant as a result of the drastic decrease in the dielectric constant [5], and the ratio of the energy barrier height to temperature can be lowered by a high temperature attainable in SCW. Chemical reaction whose energy barrier is as high as 125 kJ mol^{-1} (15 000 K) in water at $25\text{ }^\circ\text{C}$ can be accelerated by a factor of 5.4×10^{11} at $400\text{ }^\circ\text{C}$; if such a reaction is discernible on an astronomical time scale of 10 000 years in ambient water, it can be completed in one second in SCW [4]. This simple thermodynamic and kinetic consideration suggests the possibility that SCW offers an environmentally safe alternative to the use of hazardous organic solvents in various chemical processes. In this work, we attempt to disclose such a potentiality of SCW for recovering oil from polymer cracking.

The main purpose of studying how to rearrange chemical bonds between atoms by a reaction has long been confined to the development of more useful and functional materials in a more economical way. At present, furthermore, it is wanted to cultivate a new reaction path by which materials can be decomposed or transformed after their use so as to fit to the natural environment. This is important also for polymer science that has been an endeavor to synthesize polymers from monomers by mimicking and going beyond natural fibers and rubbers. Now it is necessary to study how to decompose synthetic fibers, plastics, and rubbers consumed. As illustrated in Fig. 1, polymer such as rubber occupies a stable valley on the potential energy surface constructed by the atoms (here C and H) constituting the monomers, and on the forward and backward sides, there exist two decomposed states to which polymer can be driven by SCW. Of the two possible ways, one is oxidative and the other is reductive. The latter is

Fig.1. SCW reductive pathway vs. SCW oxidative one on an energy surface.

scarcely investigated but no doubt more desirable from the global viewpoint mentioned below.

Recently, SCW oxidative decomposition of hazardous compounds in a closed system has been explored as a new treatment method for various nature-damaging compounds containing halogen atoms [1-3]. The oxidative method leads to the thorough depletion of C-H and C-C bonds and the unavoidable emission of the final product CO_2 as a source of the green house warming effect. The drawback urges us to study the SCW reductive cracking of used polymers to paraffinic oil (PO) for recycle. If we can disclose a reaction pathway where hydrogen is supplied cheaply by SCW in the transformation of such wasted and nuisance materials into an intermediate form between polymeric and monomeric ones, the CO_2 emission to the atmosphere is reduced and delayed because C-H and C-C bonds can be regained and retained, respectively. To keep clean our earth environment, it is a promising project to crack and wash the

vulcanized EPDM rubber to obtain useful PO through a reductive SCW reaction and to elucidate the hydrogen supply mechanism by applying modern NMR spectroscopy for the interesting but complicated polymer system.

2. Experimental

The rubber we investigated was synthesized by adding fillers (carbon black and paraffin) and curatives (zinc oxide, sulfur, etc.) to an EPDM polymer containing ENB (2-ethylidene-5-norbornene) as a diene monomer. The EPDM polymer used in this study consists of ethylene (68 mol%), propylene (29 mol%), and ENB (3 mol%) and has a large MW (weight average, 500 000; number average, 80 000). The components of the rubber are: EPDM (100), carbon black (80), paraffinic softener (60), zinc oxide (5), stearic acid (2), sulfur (2), and dibenzothiazyl disulfide (2); the parenthesized numerical values indicate the relative composition by weight. In our study of SCW cracking and washing, the rubber, its polymer or paraffin in the amount of 3–4 g was mixed with water (H_2O or D_2O) containing 1 mol/dm³ NaOH in a degassed and argon-filled vessel (42 cm³) which is made of Hastelloy-C276. The temperature and pressure inside the vessel were monitored directly. The SCW reaction products in the liquid phase were washed with water and *n*-hexane. The PO phase has been separated from the aqueous one by *n*-hexane and dried.

3. Results and Discussion

As shown in Fig. 2, the rubber polymer can be cracked into PO in SCW. The molecular weight (MW) of PO, which is produced by SCW cracking and extracted by *n*-hexane after the reaction, decreases with increasing temperature. At a subcritical temperature of 350 °C that is 24 °C lower than the solvent critical temperature, the product has a large MW (~100 000), which is considerably lower than that (weight average, 500 000; number average, 80 000) of the EPDM polymer itself. At a supercritical temperature of 400 °C, a desirable cracking takes place. At a higher temperature, 420 °C, PO becomes remarkably similar to the original paraffin added as a softener to the rubber, except for a weak shoulder on the larger MW side. Thus the rubber polymer chains which are cross-linked by vulcanization can be detached and cracked into PO, and the product PO has been confirmed to be useful again as a softener for the EPDM rubber synthesis. At the highest temperature (450 °C) studied here, the cracking proceeds to a larger extent as seen from a single peak at a lower MW position.

A maximum cracking efficiency is attained at 420 °C where PO and the initial paraffin are almost identical with respect to MW. The yield of PO, which is defined by the weight ratio of PO to the sum of the EPDM and the paraffin softener, amounts to ~0.9 at this optimum temperature; most of the remainder is

Fig.2. Molecular weight (MW) distribution of PO obtained from the vulcanized EPDM rubber and its original polymer by the SCW reaction. The ordinate $dW/d\log MW$ indicates the probability density, and W the weight of PO. "Paraffin" indicates the paraffin softener untreated by SCW, and 350, 400, 420, and 450 °C the reaction temperatures. R and P denote the rubber and the polymer products at the indicated temperature, respectively. The polymer cracking in water was carried out for 30 min under the following temperature (T) and pressure (P) conditions (T /°C, P /MPa): (350, 16), (400, 26), (420, 30), and (450, 38).

dissolved in water. This exceeds the formal ratio of $60/160 = \sim 0.38$ for the rubber studied here before the SCW cracking; in the rubber, the EPDM and paraffin are mixed in a weight ratio of 100 to 60 as described above. This marked difference indicates that a large fraction of PO is produced through the SCW cracking. The high yield of PO with a low residual sulfur content of < 0.1% (w/w) enables us to recycle the PO obtained by the SCW cracking for an actual rubber synthesis. Without NaOH the sulfur content was one order of magnitude higher, and such PO prevented recycle.

To prove structural changes accompanying the SCW reductive cracking, we have above analyzed the molecular weight. As the direct evidence, however, ¹³C-NMR analysis is more powerful. To find spectral correlations, we have compared the four ¹³C-NMR spectra of the relevant compounds: the EPDM polymer, the PO, the vulcanized EPDM rubber, and the paraffin softener [6]. Based on the comparison, it has been found that the spectrum of PO was composed of the spectra of the EPDM polymer and the paraffin softener. This fact clearly demonstrates that PO is composed of the softener paraffin hardly attacked by SCW and a similar paraffin generated by the SCW cracking; this is consistent with the result in Fig. 2. In other words, the essential units of the rubber are retained during the SCW processing. The main C-C-C-linkages as well as CH bonds are barely attacked by SCW, and only reactive polar bonds including S atoms, which

are minor in abundance but major in function in rubbers, are not randomly but selectively broken by the fairly mild reactivity of SCW.

We anticipate that if the SCW cracking is reductive, some of the *new, weak* peaks assignable to the methyl carbons generated by cracking are to be influenced by the addition of D supplied by SCW D₂O. Correlation of the ¹³C-NMR spectra of the PO obtained from the SCW cracking by H₂O and D₂O has been verified by expanding the spectra vertically to unveil hidden weak peaks among strong ones [6]. It has been seen that at least four CH₃ carbons shift by ~1ppm to a higher field and show triplet splitting due to ¹³C-²H coupling as a result of the ²H incorporation into the chain ends; the triplet splitting suggests a form of CH₂D. The evidence for the direct attachment of D to the terminal methyl carbons confirms such a mechanism that SCW can supply hydrogen accompanying the breakage of C-C bonds. This mechanism has been also supported the comparative ²H NMR analysis.

The total yield of the product gases was ~1% relative to the total weight of the initial EPDM and paraffin. By gaschromatography, the components and compositions are:

where the parenthesized numbers indicate the volume % of the gases under the normal conditions. A large amount of hydrogen is generated, and neither CO₂ nor CO are detected. The excessive hydrogen in the gaseous mixture supports that the SCW cracking proceeds under not oxidative but reductive conditions.

We can recycle the PO product obtained by the reductive

SCW cracking as a softener. In the actual rubber synthesis, we have compared the two compounds: one contains the PO generated by a SCW reaction at 420 °C and 30 MPa for 10 min, and the other contains the paraffin softener available commercially. As shown in Table 1, the properties of two compounds are almost the same except for deflected sample's recovery (compression set) and elongation. This is due to the similarity in the structure, the composition, and the molecular weight. The paraffin structure, which retains the main chain of EPDM, shows a good compatibility with the original polymer. The constituents have no functional groups oxidized and are good for the cure process. The molecular weight of the PO of ~1 000 provides a viscosity which is suitable for the effective lubrication required for the rubber synthesis. In the industrial production of synthesis, we can blend the PO and the softener to prevent the thermal degradation of the PO. Thus, we can reuse the PO in a cyclic manner in the rubber manufacturing without strewing the oxidative forms such as CO₂ and make a contribution to protect our environment.

4. Conclusions

Water is formed by a catalytic, photochemical or photoelectrochemical reaction between hydrogen and oxygen molecules. Although the reaction is highly irreversible under usual conditions, we can regard SCW at high enough temperatures as a source or supplier of hydrogen atoms for some chemical reactions. As a reflection of this unique feature of SCW, the vulcanized EPDM rubber and its polymer are reductively cracked in sharp contrast to the prevailing applications of SCW for oxidative decomposition of hazardous compounds. We hope that the reductive SCW cracking and washing found here take over the burning for the sake of overcoming our environmental and energy problems.

References

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Table 1. Comparison of properties of rubbers.

PO or Softener		PO	Paraffin softener
Properties			
Mooney viscometer	Viscosity, ML ₁₊₄	32	31
	Scorch, V _m	17	17
	t ₅ (min)	3.4	3.4
	t _{Δ 30} (min)	3.1	3.0
Cure meter	t _{(c)10} (min)	0.4	0.4
	t _{(c)90} (min)	1.9	1.9
	M _L (dN · m)	0.7	0.6
	M _H (dN · m)	7.1	8.2
Properties of vulcanizates	Hardness, A scale ^{a)}	57	57
	Specific gravity	1.1	1.1
	Tensile strength (MPa) ^{a)}	12.2	12.2
	Elongation (%) ^{a)}	570	490
	Tear strength (N/m) ^{a)}	4.2 × 10 ⁴	3.9 × 10 ⁴
	Compression set (%) ^{b)}	23	19

^{a)} Hardness A scale, tensile properties, and compression set according to JIS K 6301. ^{b)} Compression set indicates the recovery after heating. The lower the compression set, the better the recovery.