Depolymerization of tire and natural rubber using supercritical fluids

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Abstract

The recycling post-consumer polymers into useful feedstocks is important for both environmental and economic reasons; however, the processing of highly crosslinked polymers such as tire rubber constitutes a significant technical challenge. In this work, supercritical H_2O and CO_2 were used to controllably depolymerize tire and natural rubber. Molecular weight analysis of the degraded material indicates that reaction time can be used to control the degree of breakdown; materials in the molecular weight range of 10^3–10^4 were obtained. Also, both material composition and supercritical fluid affect the rate at which material is depolymerized. Functional analysis of the processed material shows carbonyl and aromatic groups.

1. Introduction

The recycling of post-consumer polymers into useful feedstocks is of interest for both environmental and economic reasons. Although certain polymers can be recycled easily, others may be difficult to convert to useful materials due to a high degree of crosslinking. Used automotive tires fall in the latter class; of 235 million tires discarded annually in the US, only 17% are recycled or burned for energy [1]. The tire rubber disposal problem has recently received interest both domestically and abroad.

A number of processes for feedstock recycling are currently being developed, including chemolysis, methanolysis, and catalytic cracking [2], which are to varying extents applicable to highly refractory polymers. In this work, we describe the use of supercritical fluids (SCF) as an avenue for feedstock recycling of tire rubber. The use of

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SCF as reaction media has been demonstrated for a variety of applications; several reviews on the subject are available [3–6]. Supercritical fluids have proven useful for decomposing a variety of materials, including hazardous wastes [7–10] and rubber materials [11–15]. The bulk of this work is aimed towards the degradation of waste materials into complete oxidation products or fuel feedstocks.

The experimental results presented in this research communication demonstrate the controllable breakdown of both tire and natural rubber using a SCF process. Processes to break down hazardous materials in a controllable manner may open avenues for generation of chemical feedstocks from waste material.

2. Materials and methods

Tire rubber ground to 30 mesh size was obtained from BFI Tire Recycling, Savage, MN. The natural rubber was Malaysian ribbed smoked sheet. The ground tire rubber was used as received. The natural rubber was cryogenically ground to approximately 30 mesh before processing.

Both H_2O and CO_2 were used as supercritical fluid media. The critical point for H_2O is 374 °C and 220.5 bar, that for CO_2 is 31.1 °C and 73.8 bar. For the results presented here, temperature was 380 °C and pressure was 276 bar. All experiments were conducted in a 180 ml Hastelloy autoclave (Autoclave Engineers). Reaction times varied from 0.5 to 3 h.

Samples were characterized by several methods to determine the effect of both the critical fluid and the specific reaction conditions. Molecular weight analysis was performed using gel permeation chromatography (Hewlett-Packard 1090 Chromatograph). Functional analysis was conducted using FTIR (Nicolet), NMR (Varian Unity 500), and sulfur analysis (Antek).

3. Experimental results

After supercritical fluid processing, the tire rubber samples generally result in the following product fractions, as shown in Fig. 1:

(1) an aqueous phase, if supercritical water is used,

(2) a gaseous fraction (not collected),

(3) an organic fraction, in general existing as a free layer or absorbed on the carbon black (approximately 70 wt% of starting material),

(4) a solid phase, which is principally carbon black (approximately 30 wt%); the solid phase is rinsed with methanol and with chloroform to remove the absorbed liquid organic fraction.

Supercritical processing of the natural rubber yields a homogeneous organic liquid. The carbon black content of natural rubber is low (< 1 wt%), thus no solid fraction is produced.
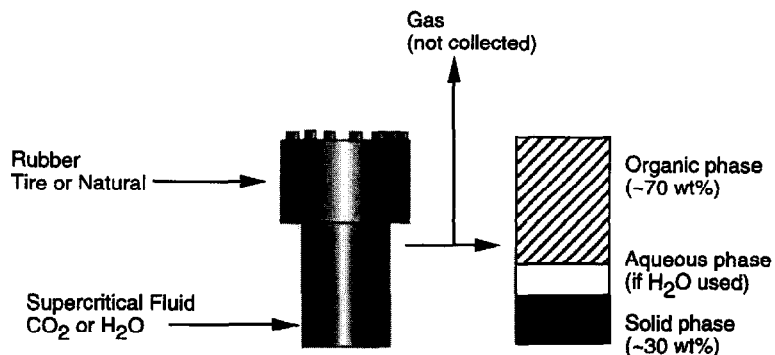
Fig. 1. Schematic of materials generated from supercritical water depolymerization of tire rubber.
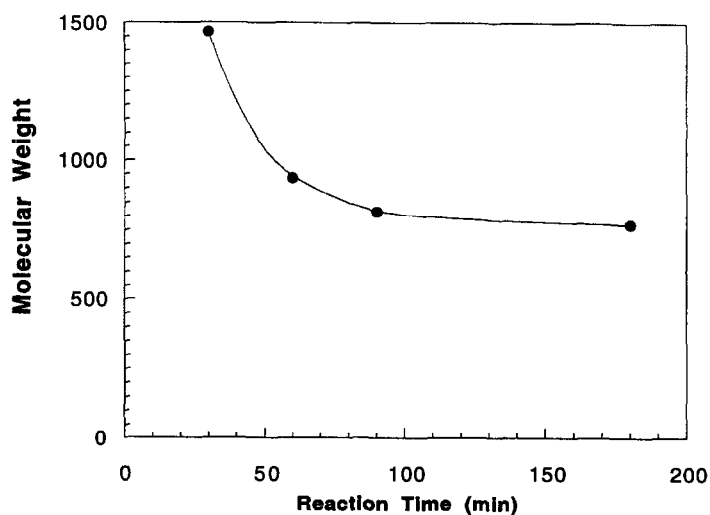

Fig. 2. Molecular weight of tire rubber versus reaction time in supercritical water. Conditions, 380 °C, 4000 psi.

3.1. Molecular weight analysis

3.1.1. Effect of processing time

The effect of time on extent of depolymerization is shown in Fig. 2. The data show an initial rapid breakdown to a level between 500 and 1000 Mw, followed by a leveling off of depolymerization rate. This curve demonstrates that processing time may be used to control the extent of depolymerization. Control over molecular weight is critical in forming products with potential value, as discussed below.

3.1.2. Natural rubber versus tire rubber

Direct comparison between tire and natural rubber was performed in both H_2O and CO_2. The natural rubber used had a starting molecular weight around 1.4×10^6; the corresponding value for tire rubber could not be obtained due to its high level of crosslinking. As shown by the results of Fig. 3, natural rubber yielded a lower molecular weight material than tire rubber for treatment with CO_2 or with water.

3.1.3. Supercritical fluid

Also shown in Fig. 3 is a comparison between the degree of breakdown achieved in supercritical CO_2 and supercritical water. The results demonstrate the more aggressive environment of supercritical water in comparison to carbon dioxide. One reason for this difference is that water acts as a much stronger nucleophile than carbon dioxide, leading to direct attack on the polymer backbone. The solvent effect of water may also play a role in supporting heterolytic reactions, as discussed below.

3.1.4. Functional group analysis

FTIR spectra for tire rubber exposed to supercritical H_2O and CO_2 showed generally similar features, as shown in Figs. 4 and 5. Major peaks appear at 2951, 2923, 1455 and 1375 cm^{-1} for samples exposed to both critical fluids. In addition, absorbances at 1708, 1602 cm^{-1} and others from samples subject to supercritical water appear; these may be attributable to carbonyl functionality. The carbonyl stretch may be associated with an acid functionality as OH groups also appear. The presence of a monosubstituted aromatic compound, possibly due to an antioxidant has also been detected.
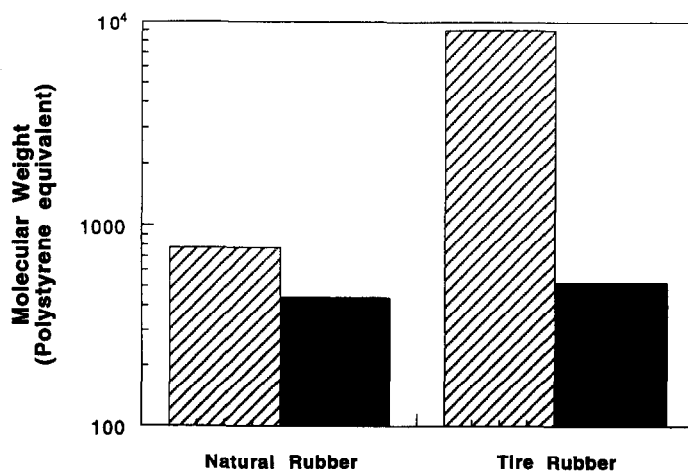

Fig. 3. Molecular weight of tire and natural rubber exposed to supercritical water ■ and CO_2 ▨. Conditions, 380 °C, 4000 psi, 3 h.
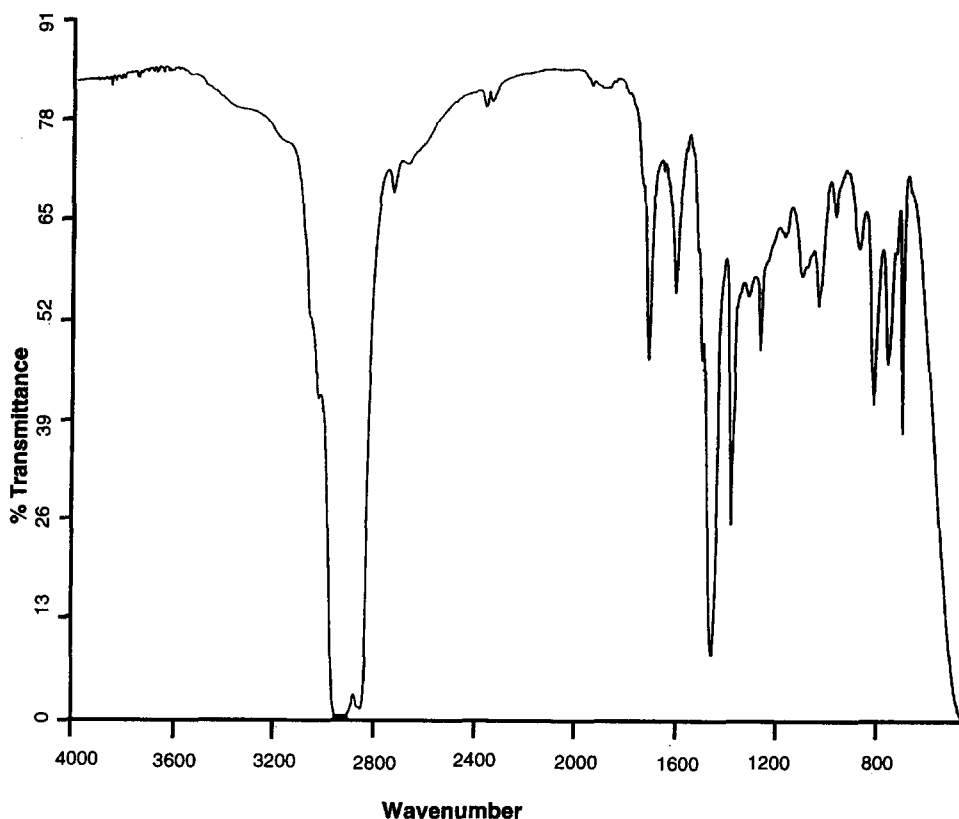
Fig. 4. FTIR spectra of tire rubber exposed to supercritical water at 380 °C, 4000 psi for 3 h.

The same major peaks appear for natural rubber as with tire rubber, with an additional peak at 814 cm^{-1}. Carbonyl functional groups are present, but to a smaller degree than with the tire rubber.

The ^{1}H and ^{13}C NMR spectra show olefinic, aromatic and aliphatic groups present in the following composition: 81 wt% hydrocarbon, 19 wt% aromatic rings, 0.4 wt% olefinic.

The organic liquid fraction of the tire rubber exposed to supercritical water contained 0.92 wt% sulfur. This result indicates that most of the sulfur is retained in the solid fraction (primarily carbon black) after reaction.

4. Discussion

The results of molecular weight analysis illustrate that SCF processing may be used to depolymerize the tire and natural rubber in a controlled manner. Selection of reaction time and supercritical fluid can be used to effect various degrees of
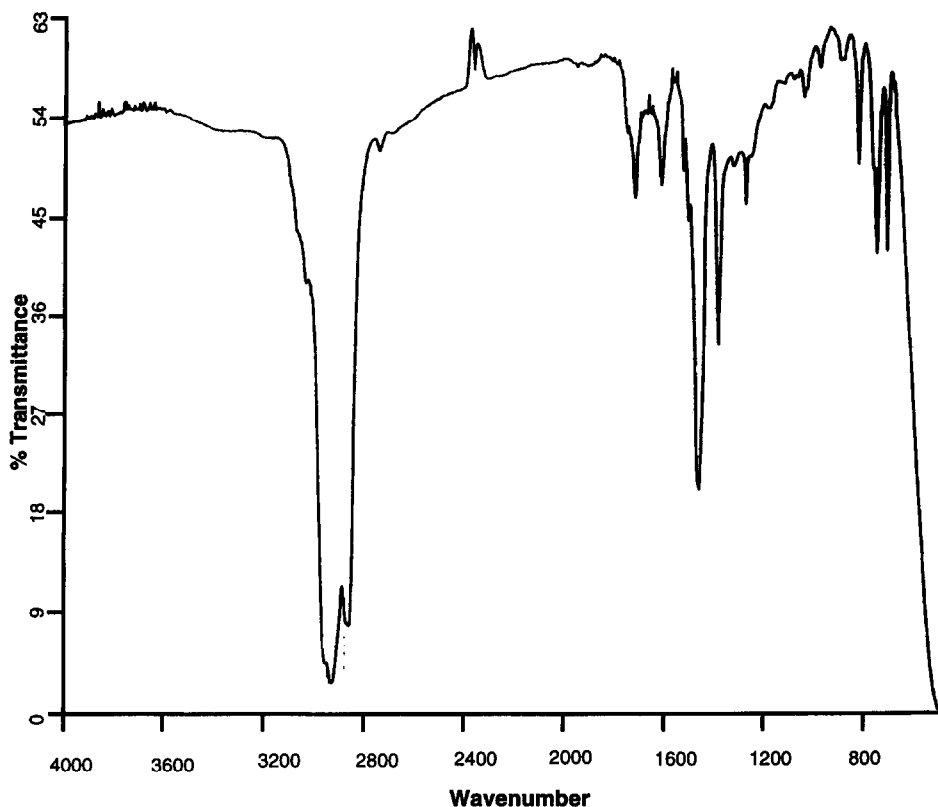
Fig. 5. FTIR spectra of tire rubber exposed to supercritical CO_2 at 380 °C, 4000 psi for 3 h.

breakdown. In order to create materials of potential value, molecular weight control may be important. In applications such as tackifiers for adhesives, the molecular weight can strongly affect product properties. Similarly, if the depolymerized product is to be used as a feedstock for another converting operation (i.e. cracking, reforming, etc.) molecular weight and uniformity are important.

Comparison between tire and natural rubber demonstrates, not unexpectedly, that different starting materials will have different behavior in the SCF environment; in this case, the heavily crosslinked tire rubber resulted in higher molecular weight material than natural rubber under the same conditions. The fact that tire rubber, one of the most refractory polymers, can be depolymerized, is a promising result of this work.

These experiments on tire rubber indicate that supercritical H_2O yields a higher degree of breakdown than supercritical CO_2. This difference may be attributable to the high dielectric constant of supercritical water, which would support heterolytic reactions and/or the direct attack of water as a nucleophile. The IR spectra, showing greater carbonyl functionality with the supercritical water depolymerized product,

also support the idea of direct attack of water as a nucleophile. The functionalization of the product using water may also be a key feature in adding value to the converted waste material.

Functional analysis yields information on the types of chemical transformations which may be effected with the depolymerized materials. The fact that some functional groups remain, e.g., carbonyl and aromatic groups, may indicate that useful components can be extracted. The olefinic contribution is small, thus direct repolymerization is probably not a viable pathway. Even at the highest degree of depolymerization, the resultant polymer chain length is approximately 40 carbon units; to build higher molecular weight units from these units, 0.4 wt% olefinic content would not be sufficient. The results of sulfur analysis indicate that the sulfur is primarily retained in the solid carbon black phase, an important feature for downstream processing.

In terms of reaction chemistry, two classes of reactions are of importance: (1) pyrolysis, via free radical chemistry and (2) hydrolysis, via nucleophilic attack. These reaction classes will yield different product slates, as they are dominated by homolytic and heterolytic pathways, respectively. Control over the ionic properties of the supercritical fluid (via pressure and temperature) may allow control over the relative importance of these different pathways, and product selectivity.

This work leaves several issues in reaction fundamentals to be resolved, including: (1) the relative rates of thermal versus heterolytic cracking, (2) the extent to which the presence of a supercritical fluid influences the activity and selectivity, (3) the effect of added oxygen and (4) the effect of catalysts on promotion of activity or selectivity. In a practical sense, the results are encouraging as SCF processing may be a viable means of breaking down highly crosslinked materials.

Acknowledgements

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