



# Primary process to fabricate functional groups on acrylonitrile-butadiene rubber surface during peroxide curing

Jing Sang<sup>a</sup>, Sumio Aisawa<sup>a,\*</sup>, Hidetoshi Hirahara<sup>a</sup>, Kunio Mori<sup>a,b</sup>

<sup>a</sup> Department of Frontier Materials and Function Engineering, Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan

<sup>b</sup> Sulfur Chemical Institute, 210, Collabo MIU, 4-3-5 Ueda, Morioka 020-0066, Japan

## HIGHLIGHTS

- We provide a innovative method to obtain functional surfaces on NBR through primary process.
- OH, C=O, COOH were fabricated on cured NBR surface during peroxide curing.
- NBR surface functional groups change with moulds surface changing.
- Reactions of NBR surface and interior are different.
- NBR surface chemical structures can be designed and controlled by moulds.

## ARTICLE INFO

### Article history:

Received 5 October 2015  
Received in revised form 11 November 2015  
Accepted 14 November 2015  
Available online 25 November 2015

### Keywords:

Primary process  
NBR  
Functional groups  
Peroxide curing  
Mould surfaces

## ABSTRACT

To satisfy the demand of low cost, shortening process and environmentally friendly products in industry, it becomes increasingly important to get functional surfaces of oxide without secondary processing of surface modification such as corona and plasma charge, especially for the soft matters of elastomeric rubber surfaces. In terms of this current rubber industry, this paper developed a surface modification method to automatically fabricate oxide functional groups on acrylonitrile-butadiene rubber (NBR) surface during primary processing using different moulds. During peroxide curing, polymer materials such as PA66, metal materials such as copper, aluminum and surface modified copper by fluoride, 4 kinds of moulds were used. Surface functional groups of cured NBR using various moulds at different curing temperature are investigated by X-ray photoelectron spectroscopy (XPS). Hydroxyl (OH), carbonyl (C=O), carboxyl groups (COOH) were fabricated on cured NBR surface. Cured NBR surface using Cu mould had the maximum concentrations of O element (9.0 at.%, at curing temperature of 180 °C). The possible surface reactions are discussed and the effects of moulds and curing temperature on NBR surface free energy have been investigated. This presented research demonstrated the reactions of NBR surfaces and interiors are different. Additionally, this surface modification method of NBR has great advantages of process, cost and thus should have a significant value to obtain functional surface in rubber industry and should have a promising future in expanding the applications of NBR.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Oxide functional groups such as hydroxy (OH) and carbonyl groups are very important to modify materials surfaces due to the reactivity of these groups as anchoring points for later process reactions on substrate materials [1]. For the materials with inactive surfaces such as rubber and plastics, OH and other hydrogen-bonding, dipoles functional groups can be obtained by performing the secondary processing of surface treatments such as plasma [2–4], UV [5], corona charge [6], etc. after shaping process. Many

applications have been already reported that oxygen plasma treatment was used to modify the plastic surfaces, for instance, to change surface wettability, to obtain the low surface energy and superhydrophobic surface properties [7], to introduce the polar functional groups such as carbonyl and carbonate groups on plastic surfaces [8]. These surface modifications are also being commonly used to improve the adhesion properties [9–11] of rubbers [12], plastics [13] and biomaterials [14].

These surface treatments are mainly important in the case of flat plates, but in the case of micro parts, large-scale parts, and complex parts with three-dimensional shape, they are difficult to take the process and in some parts cannot be used. Moreover, these physical modification methods such as plasma and corona treatments could

\* Corresponding author. Tel.: +81 19 621 6333.

E-mail address: [aisawa@iwate-u.ac.jp](mailto:aisawa@iwate-u.ac.jp) (S. Aisawa).

not create oxide groups permanently [15] because the created functional surfaces would change with time and environmental changes [16]. Additionally, after the discharge treatments the surfaces chemical bonds were destroyed to provide active sites as intermediates, since the energy of discharge is higher than the polymer chemical bond energy. The surface layers will be broken by the active sites to form very small moieties. In order to overcome this problem, it became necessary to fabricate the oxide surfaces on rubber or plastic materials without unnecessary destructives.

Although it is well known that during the shaping process of the polymeric materials the surface properties and the surface structures are affected by processing environment. In the molding process of the rubber material, the structure and characteristics of the rubber surfaces are depending on surface characteristics of the moulds contacting with the rubber. Currently, there are many reports of research focus on rubber surface visco-elastic, friction, mechanical properties [17]. The effect of different curing systems on the mechanical and physico-chemical properties of rubber bulk also has been reported [18]. However, to our knowledge, it is not cleared as yet that how does the molding process influence the chemical structure and properties of polymers surface. Especially, after curing rubbers changing from two-dimensional polymers to tridimensional polymers, it is still not clear that how do the surface structures and properties change in the different moulds during the curing. The chemical structures of rubber surfaces are not elucidated in different conditions of processing. In our previous work, formation of rubbers surface structure in vulcanizing process and surface changes in air were investigated theoretically and experimentally. It is known that vulcanized rubber surfaces are abundant in polar components when using moulds with high surface free energy, otherwise, are abundant in nonpolar components when using low surface free energy moulds [19].

Nonetheless, the effects of different-type moulds on surfaces functional groups during curing have not been investigated. And how do we use these effects should be developed. In this study, surface characteristics of cured acrylonitrile-butadiene rubbers (NBR) using various moulds during the peroxide curing are investigated. Functional groups of cured NBR surface are examined by using high-resolution X-ray photoelectron spectroscopy (XPS). 4 kinds moulds of polyamide (PA66), Al, Cu and fluorine-coated Cu were used in curing process of NBR. The influence of moulds types on NBR surface elements concentrations and surface free energy were studied. Additionally, the surface and internal reactions of NBR and interface active sites changing mechanism between moulds and NBR during the curing are discussed.

## 2. Experimentals

### 2.1. Materials and reagents

Acrylonitrile-butadiene rubber (NBR, AN: 35%, N230S, JSR Co.) compounds were made through mixing NBR (100 phr) and additives of carbon black (50 phr), stearic acid (1 phr), stabilizer ZnO (5 phr). The curing agent, dicumyl peroxide (DCP, reagent grade) was added to the base compounds above. Polyamide (PA66, 2015B, 230 °C/451 kPa, Ube Industries, Ltd.), Al (AL-013322, Nilaco, Co., Ltd.), Cu (CU-113321, Nilaco, Co., Ltd.) and fluorinated Cu films were used as NBR curing moulds. Fluoride compound of 6-(N-Allyl-1,1,2,2-tetrahydroperfluorodecyl)amino-1,3,5-triazine-2,4-dithiol monosodium was used as Cu surface treatment agent (Sulfur Chemical Institute Co., Ltd.).

### 2.2. Compounding and curing

Uncured NBR compound sheets were obtained through mixing NBR raw rubber, filler, stearic acid and ZnO by banbury mixer

and adding DCP to the NBR master batch on two rolls mill. After blending, uncured NBR compound sheets were molded being folded between two films of 4 different materials as moulds in rheometer cabinet at 140 °C, 150 °C, 160 °C, 170 °C, and 180 °C for 30 min (Fig. 1(a)). The cured NBR samples were immediately removed from the rheometer cabinet. The surfaces and cut-surfaces of cured NBR rubbers for analytical samples were prepared as  $1 \times 2 \times 5$  mm with six surfaces. One surface contacted with mould is surface obtained by curing and the others are cut-surfaces (interior) obtained by cutting which mean bulk cured NBR characteristics. Before analysis various mould films were peeled from cured NBR keeping 24 h in vacuum (Fig. 1(b)).

### 2.3. Measurements

The surfaces and cut-surfaces chemical compositions and structures of cured NBR rubbers were analyzed by XPS (PHI QUANTERA ESCA system) with Multi Technique Spectrometer, focusing monochromator (ULVAC-PHI Inc.) and Al K $\alpha$ X-ray source of  $100 \mu\text{m} \times 100 \mu\text{m}$  spot. Pass energies of the analyzer were 69 eV for high-resolution scans at 300 W. The angle resolved measurements were made at an electron takeoff angle of  $\theta = 45^\circ$ . The electron flood gun was used for charge neutralization, and the analysis chamber was remained at  $3.0 \times 10^{-6}$  Pa in the whole XPS measurement. The XPS spectra were subjected to Shirley background subtraction formalism and the data was using the saturated C1s peak at 284.8 eV during chemical-bonding-state assignments. The full width at half maximum (FWHM) of C-C/C-H component was left to vary freely then the other components were fixed to adopt this value. During all the fitting curve treatments, Gaussian-Lorentzian lines of variable proportion were used and the XPS experimental curve fitting process was taken by Mutipak software.

Static contact angles were measured by optical contact angle measuring instrument (Kyowa Interface Science DM-501) with 1  $\mu\text{L}$  distilled water,  $\alpha$ -Bromo naphthalene, diiodomethane at ambient temperature. Contact angle average value of 5 measurements at different positions in one sample was adopted as the contact angle. Surface free energy was calculated from the 3 kinds of liquid contact angles by Fowkes-Owens formula.

## 3. Results and discussion

### 3.1. Effect of moulds and curing temperature on surface element composition

It has been known that hydrocarbons bonds of rubber have unstable portions, which have a significant influence on the thermal reactions. Especially, the unstable portions of the rubber like NBR with the unsaturated hydrocarbon groups could be decomposed and reacted to the peroxide radicals when the rubber exposed to high temperature [20]. However, those oxidation reactions have been mainly investigated in the field of thermal deterioration of rubber [21]. Herein, we utilize the oxidation reactions and the characteristics of NBR with different polarity portions of nitrile groups and butadiene groups to fabricate functional groups on NBR surface during the peroxide curing. At the same time, the interaction between NBR and moulds, and the effect of mould on the characteristic of cured NBR were determined. The surface elemental component ratios of the cured NBR surfaces using various moulds at different curing temperature were examined by XPS (Fig. 2). Calculated from the recipe of uncured rubber master the elemental component ratios are C: 93.6%, N: 6.2, and O: 0.2%. O is from the DCP peroxide. After curing, O contents are much more than the calculated value of 0.2% at any curing temperature and moulds (Fig. 2(a)). These results indicate that the oxide reaction

Download English Version:

<https://daneshyari.com/en/article/145943>

Download Persian Version:

<https://daneshyari.com/article/145943>

[Daneshyari.com](https://daneshyari.com)