Preparation and Properties of Iodine-Doped Radiopaque Natural Rubber

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ABSTRACT: Polymers exhibit low electron density and they are radiolucent. Polymers can be made radiopaque by different techniques. We report a method for the preparation of radiopaque material from natural rubber (NR). NR in its latex form was iodinated. Iodinated natural rubber (INR) was characterized by using UV, thermo gravimetric analysis (TGA), and X-ray images. INR was compounded at high and low temperatures and its physical properties were measured. The low temperature cured samples show good radiopacity and conductivity. The optical density of low temperature cured samples was measured. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 429–434, 2007

Key words: radiopacity; radiopaque polymers; iodinated natural rubber; optical density

INTRODUCTION

Radiopacity is a desirable property of implants used in dentistry.[1] Nowadays radiopaque polymers are of interest to medicine and dentistry because of their wide area of applications such as catheters, surgical tools, dental products, medical tubing's, etc. When used to produce medical devices for insertion into the body for diagnostic or surgical procedures, the additives in radiopaque compounds render the devices visible under fluoroscopy or X-ray imaging. The additives, or radiopacifiers, attenuate energy differently than surrounding body tissues, providing the contrast in X-ray image. Research into radiopaque polymers explores methods of increasing average electron density and the specific gravity of polymer by incorporating heavy elements into these systems. The radiopaque compounds can be formulated using a variety of thermoplastic polymers and additives to customize a product's specific gravity and physical properties (such as flexural modulus, tensile strength, and impact strength) for specific end-use requirements. The type and amount of additives depends on the base resin and on the wall-thickness, surface smoothness, color, and other desired properties of the application. Among the most widely used radiopacifiers are barium sulfate, bismuth halideszirconium dioxide, and tungsten.[2–6]

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Polymers could be rendered radiopaque by blending them with radio pacifying agents. However the physical and mechanical properties of the base polymer are often adversely affected by the incorporation of these additives.[7] Another approach to make the polymer radiopaque is to covalently link a radio contrast dye to the polymer. This approach is possible only if the polymer possesses a reactive functional group to which the dye could be attached. The best method to produce radiopaque polymers is to synthesize reactive monomers having covalently bound heavy atoms and use these monomers as building blocks for new polymeric biomaterials that exhibit intrinsic radiopacity. Several iodine-containing compounds like iopanoic acid {3-(3-amino-2,4,6-triiodophenyl)-2-ethyl propanoic acid} and isothalamic acid (5-acetamido-2,4,6-triiodo-*N*-methyl isophthalamic acid) are clinically used as nontoxic radio contrast materials. In view of the fact that iodine is a heavier atom compared to bromine, and since iodine containing dyes are routinely used in interventional radiology, attempts were made to synthesize iodine containing compounds as well as monomers.[8,9]

Here we had made an attempt to prepare radiopaque NR using iodination. NR has been chosen for its excellent properties, such as good mechanical properties, low cost, and easy availability. These are the major advantages of NR, which makes it dominant in many urinary catheters industrial, automotive, engineering, and medical applications. In medical field, it finds various applications such as medical tubes, surgical gloves, etc. In this report, NR was

TABLE I
Compounding Formulation of INR/NR

Components	Mix A (phr)	Mix B (phr)	Mix C (phr)	Mix D (phr)	Mix E (phr)
NR	100	90	75	50	0
INR	0	10	25	50	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
CBS	0.6	0.6	0.6	0.6	0.6
TMTD	0.1	0.1	0.1	0.1	0.1
Sulphur	2.5	2.5	2.5	2.5	2.5

iodinated, cured at high and low temperatures, and its properties were measured.

EXPERIMENTAL

Materials

Centrifuged latex of 60% DRC was diluted to 30 DRC and was used for this study. Iodine, potassium hydroxide, and potassium iodide were from S.D. Fine-Chem, Mumbai.

Preparation of INR

Centrifuged latex was stabilized by stirring with a mixture of 10% KOH, 10% potassium oleate, and vulcastab VL for 3–4 h. It was then acidified with 1*N* HCl. The acidified latex was iodinated and the coagulam was washed several times with water and then dried at room temperature.

Iodinated natural rubber (INR) was characterized using ultraviolet spectrophotometer (using Carry 5000 instrument) and thermogravimetric analysis (TGA Q-50).

In vitro analysis of antibacterial property

To prepare the microorganism for the experiment, the organism was subcultured on to agar plates and incubated overnight at 37°C. Antimicrobial properties were assessed by using zone inhibition method. For that small pieces of iodinated coagulam and control were plated separately onto agar plates streaked with *E. coli*. Plates were incubated at 37°C for 24 h, and were examined to see if a zone of inhibition had been produced around the pieces.

Compounding and physical properties

The INR compound was prepared on a laboratory mixing mill (6 in. × 12 in.) as per the formulation given in Table I. The optimum cure times of the compound was determined using a Goettfert elastograph model 67,085 as per ASTM D 1646 (1981) at a temperature of 150°C. The compound was compression molded at 150°C in an electrically heated hydraulic press into 1 mm thick sheets. For this, the mold was preheated to 150°C, and a piece of preformed material was placed directly in the mold cavity and compressed under a hydraulic clamp pressure of 200 kg/cm^2. Upon completion of the required cure cycle, the pressure was released and the sheets were stripped from the mold and suddenly cooled by plunging into cold water. After a few seconds, the sample was taken from water and was dried. Dumbell shaped tensile test specimens were punched out of the compression molded sheets along the mill direction. The tensile properties of the INR vulcanizate was evaluated on a Zwick universal testing machine using a cross head speed of 500 nm/min, according to ASTM D 624. The compression molded sheet was cut in to round shape to measure the radiopacity. INR was also compounded at room temperature using zinc isopropyl xanthate using the compounding formulation given in Table II.

Cure time determination

Cure characteristics and the rubber-filler interaction have been studied using a Rubber Process Analyzer (model-RPA200, Alpha Technologies).The die type used was biconical and the die gap was 0.487. The cure time of the high temperature cured samples were determined at 150°C at a frequency of 50.0 and strain of 0.20°.

Compression molding

Blanks cut from unvulcanized sheets marked with the machine direction were vulcanized at a temperature of (150 ± 2)°C in the case of high temperature cured samples and at a pressure of 200 kg/cm^2 in an electrically heated hydraulic press to their respective cure times. Rectangular moldings were cooled quickly in water at the end of each curing cycle and were used for subsequent property measurements. The low temperature cured samples are made at low

TABLE II
Compounding Formulation for Low-Temperature Curing of INR

Ingredients	Mix A (phr)
Iodinated NR	200
ZnO	10
Stearic acid	4
ZDC[a]	5
Sulphur	5
Zinc isopropyl xanthate	3.5

[a] Zinc diethyldithio carbamate.

temperature by keeping the sample in a hydraulic press at a pressure of 200 kg/cm^2 at room temperature for 24 h.

Mechanical properties

Dumbbell shaped tensile specimens were punched out from the vulcanized sheets and the mechanical properties were studied using a Shimadzu Universal Testing Machine (Model-AGI) with a load cell of 10 kN capacities as per ASTMD421-68. The gauge length between the jaws at the start of each test was adjusted to 30 mm and the measurements were carried out at a cross head speed of 500 mm/min.

Conductivity measurements

D.C. conductivity of the samples was measured using Keithley nanovoltmeter (model 2400 series) at room temperature using four-probe electrode configurations. The samples had dimensions 60 × 20 × 3 mm^3. The thickness of the specimens was measured using a thickness monitor.[6]

By applying voltage, the corresponding current is obtained and the conductivity is measured using the equation

$$\sigma = I/dV$$

where I is the current, d is the thickness of the film, and V is the voltage.

Radiopacity studies

Radiopacity of different systems were studied using a general clinical X-ray instrument of 40 kV energy and 2 mille ampere current. A clinical general X-ray instrument is commonly used for obtaining two-dimensional image of patient's anatomy by using X-ray film as detector. In this technique, the radiation from X-ray tube is transmitted through the material and reaches the film. After processing the film, the radiograph is obtained. The radiograph is a negative image. With increase in thickness of the sample, the concentration of iodine in the sample increases and hence radiopacity increases.

Optical density measurements

The term density refers to the degree of blackening of the film. The degree of blackness is directly related to the intensity of radiation. The measurement of blackness is called photographic density or optical density (OD).

$$\mathrm{OD} = \log_{10}(I_0/I_t)$$

where (I_0/I_t) is the light stopping effect or opacity. I_0 is the light intensity incident on the film and I_t is the light transmitted through the film. The optical density can be measured using a densitometer. The transmittance is the fraction of I_t/I_0 of incident light passing through the film. As OD increases transmittance decreases. The optical density of X-ray films were measured using a Calden densitometer.

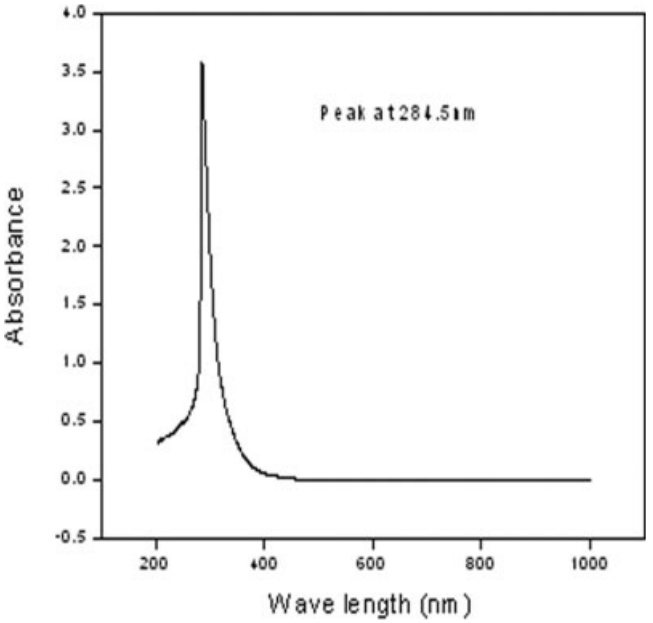

Figure 1 UV spectroscopy of iodinated natural rubber.

RESULTS AND DISCUSSION

Characterization

Iodinated rubber was prepared in the latex stage using iodine solution. Figure 1 shows the UV spectrum of INR in toluene scanned at 200–700 nm regions. The spectrum shows a sharp peak at 284.5 nm. Methyl iodide has absorption maxima of 258 nm.[10] Due to the presence of additional methylene groups in INR, its absorption maxima was shifted to 284.5 nm, confirming iodination of NR.

The TGA thermogram of NR and INR is shown in Figure 2. A peak observed with a peak max. at 171.57°C was because of the elimination of I_2. The onset of this decomposition was found at 138.37°C and at 150°C around 1.5% of degradation takes place. A second peak max. at 444.19°C was observed because of the decomposition of NR. The onset of this decomposition is noted at 331.33°C and corresponds to a weight loss of 15.9%.

Figure 3 shows the positive print of X-ray photographs of INR. It was clear from the figure that the INR shows good radiopacity. NR contains only carbon and hydrogen. Hence it is radiolucent in nature.

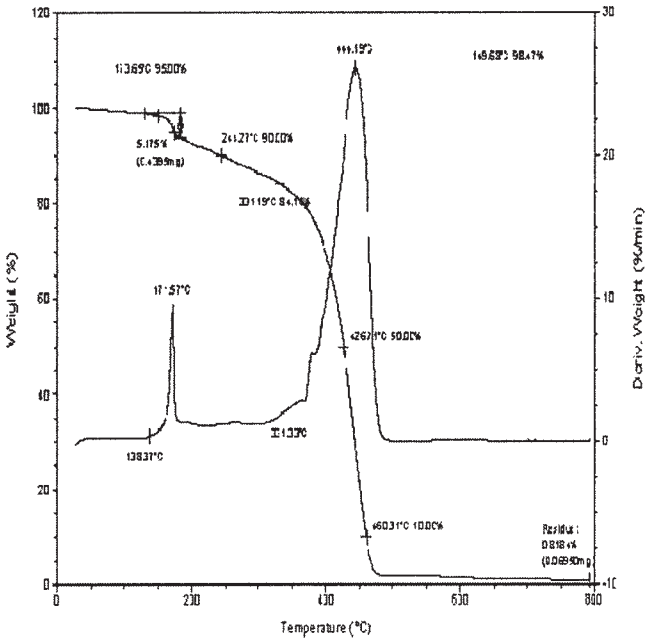

Figure 2 Thermogravimetric diagram of iodinated natural rubber.

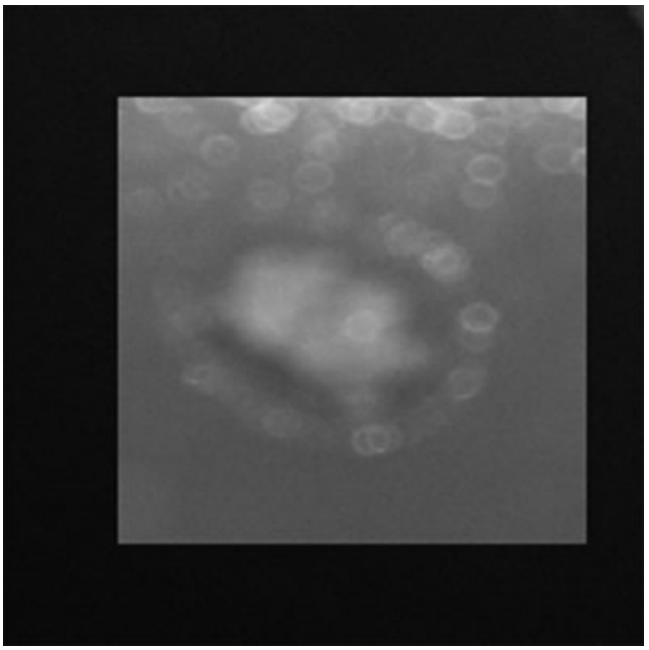

Figure 4 A clear zone of inhibition from *in vitro* analysis of antibacterial property in the INR sample.

Antibacterial property

A clear zone of inhibition was visible in the case of iodinated rubber. A wide disparity in colony counts between INR and NR was observed. The effectiveness of antibacterial activity depends on the availability of free iodine that subsequently binds to the bacteria. The studies show that NR containing iodine is antibacterial in nature. Figure 4 shows a clear zone of inhibition in the INR.

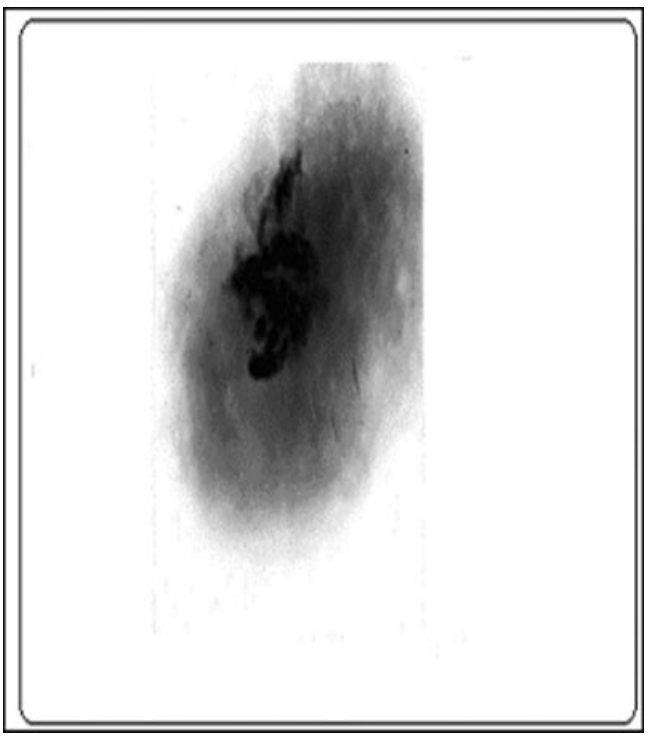

Figure 3 The positive print of X-ray photograph of iodinated NR.

Physical properties

INR is blended with NR in different proportions and its physical properties were measured. The physical properties of INR compounds (mix A, B, C, D, and E) are shown in Table III. The tensile strength and tear strength were found to decreases with increase in concentration of INR. This may be because of the less sulfur crosslinks and because of the presence of iodine, which have an acidic nature. The physical properties of low temperature cured samples are shown in Table IV. The tensile strength and tear strength were found to be high compared to high temperature cured sample. At high temperature, some of the sulfur crosslinks may break and the room temperature curing will increase the effective crosslinks, which inturn increases the physical properties.

TABLE III
Physical Properties of NR/INR Blends

Property	Mix A	Mix B	Mix C	Mix D	Mix E
Tensile strength (MPa)	22.4	18.4	17.5	16.2	15.2
Tear strength (N/mm)	44.8	36.8	35.2	34.9	30.6
Elongation at break (%)	2789.3	2291.3	2236.4	2210.2	1930.1

TABLE IV
Physical Properties of Low-Temperature Cured Samples

Tensile strength (MPa)	18.76
Tear strength (N/mm)	37.62
Elongation at break (%)	1840

Radiopacity measurements

The high temperature cured INR does not show radiopacity because of the elimination of iodine. Figure 5 shows the positive print of X-ray photographs of low temperature cured samples with different thickness. It is clear from the figure that the sample with higher thickness gives better radiopacity. At higher thickness, the concentration of iodine is high and hence the electron density also high. The radiopacity increases with increase in thickness of the samples. When the NR is iodinated, its electron density increases and hence shows good radiopacity.

Optical density measurements

The variation of optical density with thickness of the sample is shown in Figure 6. When the thickness of the sample increases the optical density decreases, because it is inversely related to the radiopacity.

The optical density of INR samples were compared with lead sheet having a thickness 2 mm and is shown in Table V. From this table it is clear that after iodination optical density of NR decreases, and 3.35 mm sample possess an optical density of 0.76. By the incorporation of more iodine to NR we can further decrease the optical density. When the concentration of iodine in NR increases, the optical density decreases, which in turn increases the radiopacity of the sample. As such, radiopaue INR with higher thickness could be used for shielding applications.

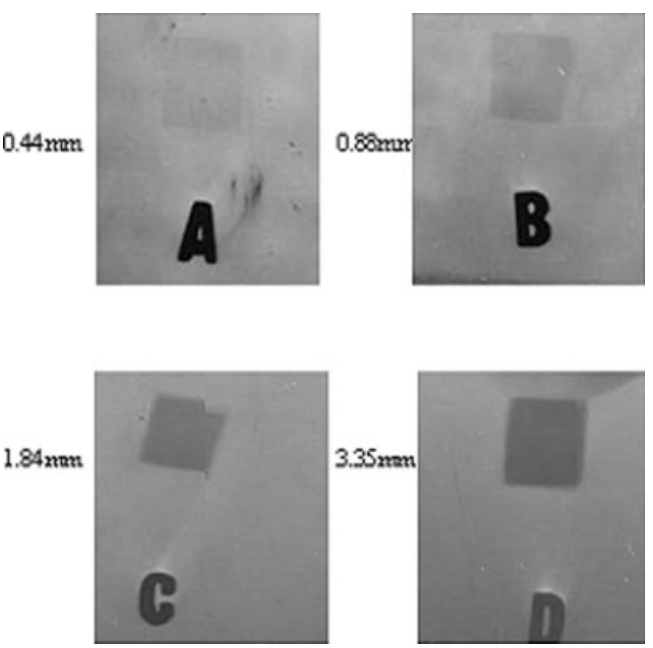

Figure 5 The positive print of X-ray photographs of low temperature cured samples of various thickness.

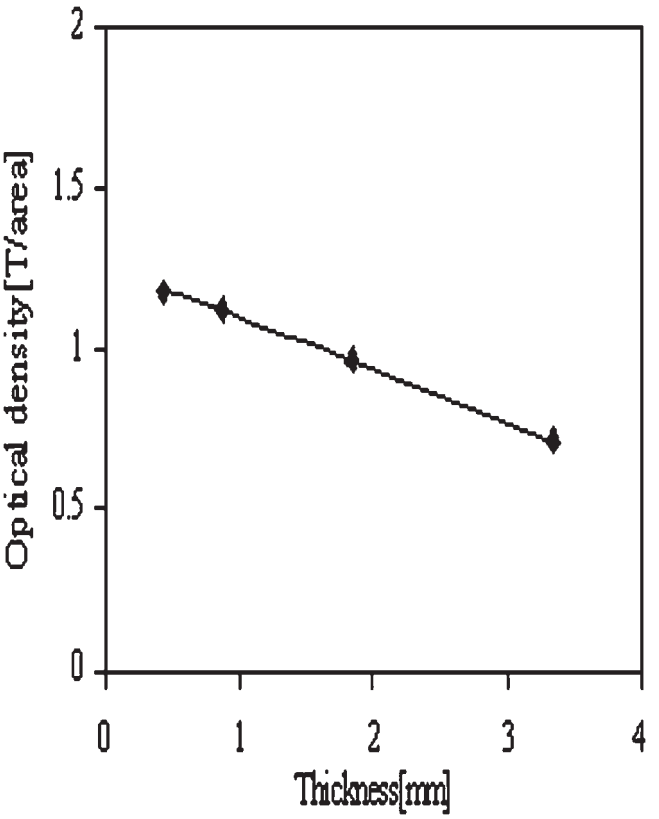

Figure 6 The variation of optical density with thickness of the sample.

DC conductivity

D C conductivity of the low temperature cured sample was in the order of 7.32×10^{-7} S/cm as shown in the I-V plot of low temperature cured sample (Fig. 7). The conductivity of NR increases because of the presence of iodine.

CONCLUSIONS

Radiopaque NR can be prepared by the iodination of NR. Low temperature cured INR shows better

TABLE V
Optical Density of Various Samples

Sample	Optical density
NR	1.26
INR	0.76
Lead sheild	0.18

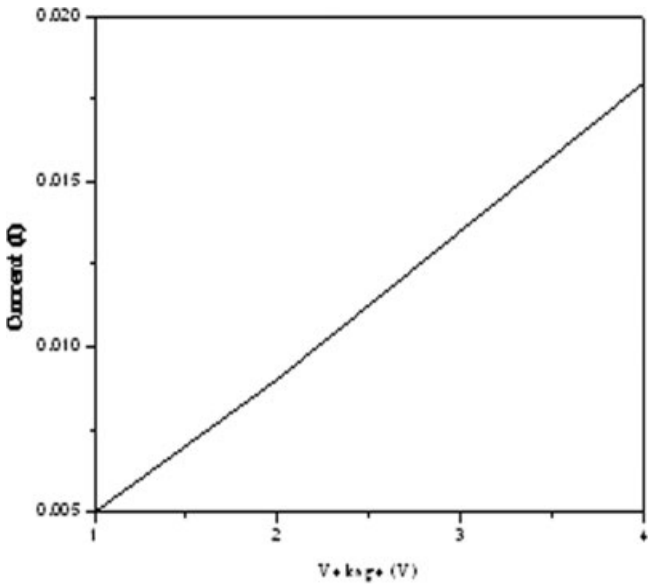

Figure 7 I-V plot of low temperature cured sample.

radiopacity than high temperature cured sample. INR shows excellent antibacterial property. The radiopacity of the INR is found to be dependent on the thickness of the sample and it increases with increase in thickness. The optical density of the INR is found to decrease with the increase in thickness of the sample. The D.C. conductivity of the INR sample is found to be in the order of 7.32×10^{-7} S/cm.

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