Hydrogenation of Nitrile Rubber Using a New Homogeneous Palladium (II) Catalyst: Synthesis and Characterization

INTRODUCTION

Butadiene-acrylonitrile rubber (NBR), being polar, is an oil and solvent resistant rubber and particularly gives resistance to nonpolar solvents. But due to the presence of diene part, it is more susceptible to thermal and oxidative degradation than saturated elastomers. It can however be made more resistant to heat, ozone, and light by hydrogenation.

Saturated nitrile elastomers (HSN) have been marketed recently by Nippon Zeon Co. (ZET-POL), Bayer (THERBAN), and Polysar (TORNAC).[1-3] They have different grades depending on degree of unsaturation. The methods of hydrogenation of nitrile for making HSN is however not disclosed. Weinstein[4] reported the synthesis of an elastomeric tetramethylene-ethyl ethylene acrylonitrile copolymer by hydrogenation of nitrile rubber using Rhodium Catalyst. Kubo et al.[5] discussed structure and properties of highly saturated nitrile elastomer. Schulz discussed various chemical modifications of rubbers.[6] Mohammadi and Rempel reported catalytic hydrogenation, hydroformylation and hydroxymethylation of polybutadiene.[7]

In the present work, a noble synthetic method was adopted for the hydrogenation reaction of nitrile elastomers using homogeneous catalyst system. Six-membered cyclopalladate complex of 2-Benzoyl pyridine was used as catalyst. The acrylonitrile content (ACN) of the NBRs was varied from 33% to 51%. The hydrogenation reaction was also carried out for carboxylated nitrile rubber (XNBR) and Polybutadiene rubber (BR) under identical condition for comparison. The advantage of this kind of reaction is that it can be stopped at any stage to get the desired degree of hydrogenation. The reaction was carried out at two different pressures, times and temperatures by keeping the same catalyst concentration. The reaction products were characterized.

EXPERIMENTAL

Materials

Six-membered cyclopalladate complex of 2-Benzoyl pyridine [{Pd (PCPh) (OAc)}$_2$] 0.25 CH$_2$Cl$_2$ was prepared. Chloroform and chlorobenzene were obtained from E. Merck (India) Limited.

A high pressure rocking autoclave (High Pressure Equipment Co., USA) of 300 mL capacity at 298K and atmospheric pressure having an angular play of 15° with 30 oscillations min^{-1} was used. The autoclave is electrically heated externally and controlled by means of a Sunvic thermo-regulator.

Nitrile rubber of varying ACN contents 33%, 40%, and 51% were used as substrates for hydrogenation. These were obtained from B. F. Goodrich Chemical Co., USA. XNBR and BR were obtained from Polysar, Canada and Indian Petrochemical Corporation, India, respectively. Zetpol, NEM 2000 of ACN content 37% was obtained from Nippon Zeon Co. Ltd., Tokyo, Japan.

PROCEDURE

Preparation of the Catalyst

Cyclopalladate complex, a yellow crystalline solid was prepared by refluxing an acetic acid suspension of Palladium (II) acetate and 2-benzoyl pyridine.[8] Palladium (II) acetate was obtained by dissolving Pd sponge suspended in hot glacial acetic acid by addition of minimum quantity of HNO$_3$.[9]

NBR Hydrogenation

Solution of 5 g samples of NBR substrates in 100 mL of CHCl$_3$ and 0.3 m mole of catalyst were introduced into a glass liner in order to minimize the corrosion inside the autoclave. The liner was

TABLE I

Rubbers Hydrogenated in Chloroform at a Catalyst Concentration of 0.3 m mole
at 50°C Under a Pressure of 0.7 MPa for 3 h

	ACN content
NBR I (A)	33%
NBR II (B)	40%
NBR III (C)	51%
XNBR (D)	34%
BR (E)	—

placed into the autoclave and hydrogen gas was passed through it up to a pressure of 0.7 MPa. The autoclave was then heated slowly to 50°C and the temperature was maintained constant for 3 h with the rocking of the reactor for the same period. The temperature, pressure and time were varied subsequently. After the end of the specific time period the autoclave was allowed to cool down to room temperature.

The reaction mixture was then taken out of the autoclave and the polymer was coagulated into methanol, washed with methanol and hexane several times and finally dried in vacuum.

CHARACTERIZATION

The number of double bonds reduced was determined by iodine value as per JIS 0070 (Japanese Industrial Standard).

The glass transition temperature was measured by Differential Scanning Calorimetry (DSC) using DuPont model 910.

Studies in NMR and IR Spectroscopy were carried out using a Varian EM-390 Spectrometer on 90 MHz and Perkin Elmer 843 Spectrophotometer, respectively.

Sol-gel analysis was carried out by taking 0.2 g of the sample and dissolving in chloroform. The concentration of the aliquot portion of the sol was determined by evaporating the solvent.

The green strength of raw rubbers was determined by cutting dumbbell (dimension as per ASTM D 3183) from thin sheet of 0.80 mm thickness. The stress-strain curves were obtained in a Zwick UTM 1445 at room temperature at a rate of 500 mm/min.

RESULTS AND DISCUSSION

The hydrogenation reaction was carried out at different temperatures and times. The conditions of hydrogenation are stated in Tables I and II. Table III reports the characteristics of the hydro-

TABLE II

Conditions for Hydrogenation at a Catalyst Concentration of 0.3 m mole and 5.6 MPa Pressure
and the Iodine Value of Hydrogenated Rubbers

Copolymer	ACN content	Temperature (°C)	Time (h)	Solvent	Iodine value (g/100 g)
NBR I	33%	75	6	$CHCl_3$	50
	33%	70	3	$CHCl_3$	70
	33%	70	3	C_6H_5Cl	55
	33%	50	6	$CHCl_3$	75
NBR II	40%	90	3	C_6H_5Cl	55
	40%	50	20	$CHCl_3$	90
	40%	55	4	$CHCl_3$	60
NBR III	51%	50	16	$CHCl_3$	80
XNBR	34%	50	3	$CHCl_3$	100

TABLE III
Characterization of Rubber Samples

Sample reference	Copolymer	ACN content (%)	I$_2$ value (g/100 g)	T$_g$ (°C)	Gel content (%)
A	NBR I	33	303	−25	1.0
A′	HNBR I	33	101	−28	1.2
B	NBR II	40	300	−18	1.1
B′	HNBR II	40	92	−22	1.0
C	NBR III	51	295	−11	9.1
C′	HNBR III	51	90	−16	9.8
D	XNBR	34	308	−23	2.0
D′	HXNBR	34	104	−25	2.3
E	BR	—	320	−100	0.0
E′	HBR	—	98	−103	0.0

genated products. It is observed from Table III, that the iodine value decreases to about one third for all the NBR samples. The amount of hydrogenation at a particular time and temperature is independent of the acrylonitrile content. All three NBR samples give iodine value about 100 after hydrogenation. XNBR and BR with approximately same number of double bonds show identical hydrogenation efficiency. IR spectra shows that on hydrogenation using the new catalyst, there is no reaction with the —CN group (there is no —NH$_2$ peak at around 3500 cm^{-1}). NMR data supports hydrogenation at the double bonds.

The glass transition temperatures (T$_g$) from DSC are reported in Table III. T$_g$ decreases on hydrogenation for NBR with 33% ACN content. This is also true for samples containing 40 and 51% ACN. Figure 1 shows such a plot. Similar results were obtained by Kubo et al.[5] on hydrogenation of nitrile rubber at higher nitrile content. The lower T$_g$ on hydrogenation indicates flexibility of the chain due to replacement of the rigid double bonds in the backbone by freely rotating single bonds.

Gel content, however, does not change on hydrogenation (Table III) for all the samples studied. NBR with low ACN content has about 1% gel, whereas XNBR contain about 2% gel.

The stress-strain properties are reported in Figures 2–4. For comparison the properties of a commercial material (ZETPOL 2000) is also plotted. As usual, the samples with higher acrylonitrile content show higher breaking stress. With 51%, the maximum stress recorded is 3.96 MPa. The value of breaking strain is highest for nitrile rubber with 40% ACN content. On hydrogenation, the tensile strength is significantly improved. The higher the acrylonitrile content the higher is the improvement. There is 49% increase in green strength for 40% ACN sample. The breaking strain increases for samples with 33% and 40% ACN contents, but decreases for 51% ACN sample. The small strain modulus also increases on hydrogenation for all the samples. The commercial material ZETPOL with very low iodine values of 5 (much higher level of hydrogenation than our sample) shows better stress-strain properties. The data on counterpart non-hydrogenated NBR is not available for comparison.

Stress-strain behaviours of XNBR and BR are also shown in Fig. 3. BR sample shows a great improvement in both ultimate strain and breaking stress, whereas XNBR shows marginal improvement.

By changing the reaction condition, however, the stress-strain properties could be significantly changed (Fig. 4). The increase in tensile strength for NBR samples with 33%, 40% and 51% ACN content is probably due to more regularity and flexibility of the chains.

The mechanism of hydrogenation using the new catalyst system may be proposed as follows in line with earlier work.[10] The catalyst first reacts with hydrogen to form metal hydride. This transfers two hydrogen atoms to C—C double bond as shown in Scheme A. The successive (or possibly simultaneous) transfer of hydrogen atoms to the olefinic double bond site depends upon the ability of the catalyst to convert unhindered olefins. It may be proposed that the free double bonds are hydrogenated first. As a result the 1,2 segment of butadiene gets saturated before the 1,4 segments.
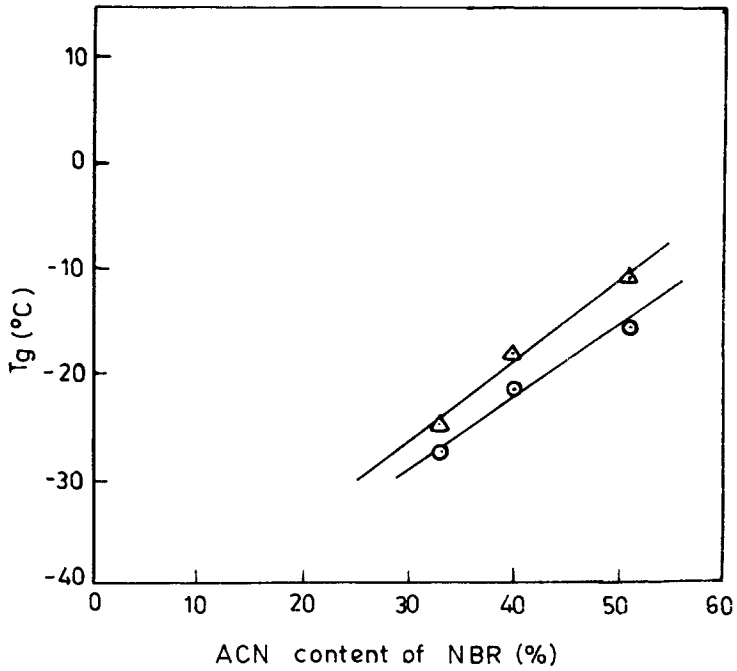
Fig. 1.   Effect of ACN content on glass transition temperature (T_g) of different NBR substrates: △ - NBR; ⊙ - HNBR.
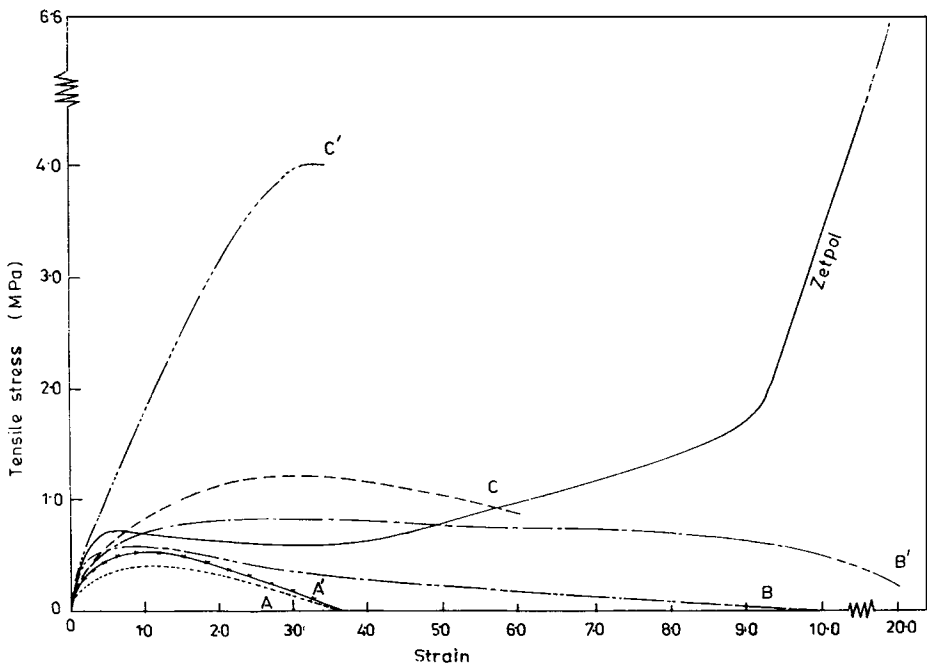

Fig. 2.   Stress-strain curves of NBR with varied ACN content and their hydrogenated products (A', B', C').
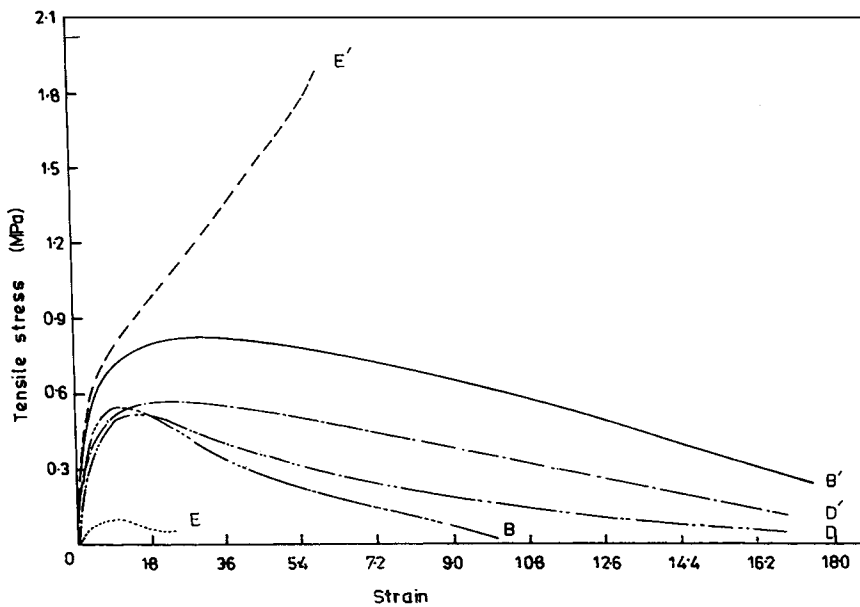
Fig. 3.   Stress-strain curves of different polymers with corresponding hydrogenated products.
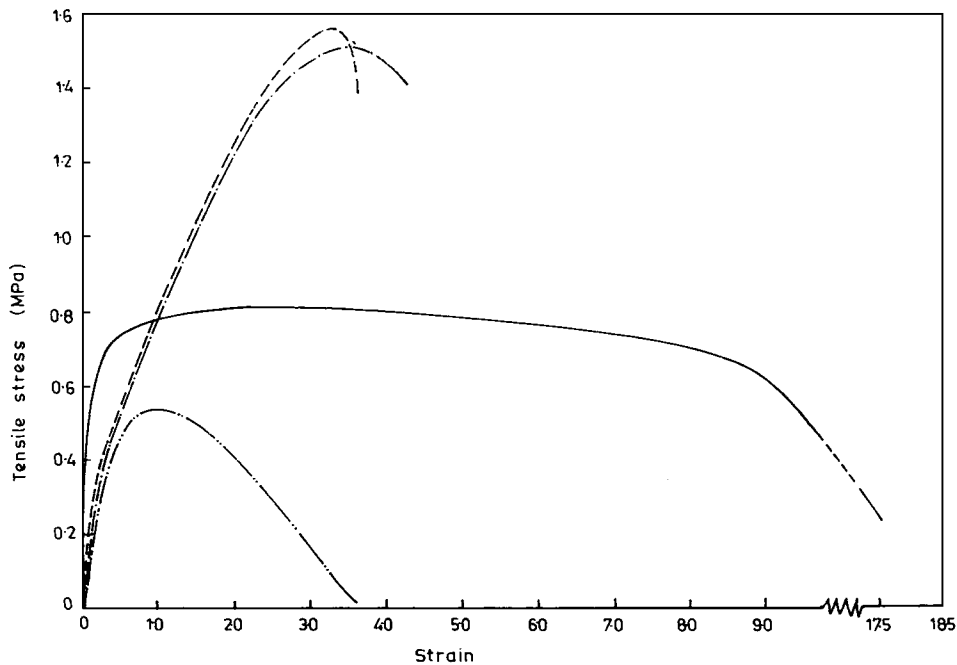

Fig. 4.   Stress-strain curves of the hydrogenated polymers.

– · · – HNBR I

——— HNBR II

— ·· — HNBR (33%, 5.6 MPa, 70°C, C_6H_5Cl)

— · — HNBR (40%, 5.6 MPa, 55°C, $CHCl_3$)

A similar proposition without mechanism has been given by Kubo et al.[5] for their systems. The principal advantage obtained by homogeneous Pd catalyst is its degree of selectivity for reducing only isolated C—C double bonds, even in the presence of functional groups as nitrile.
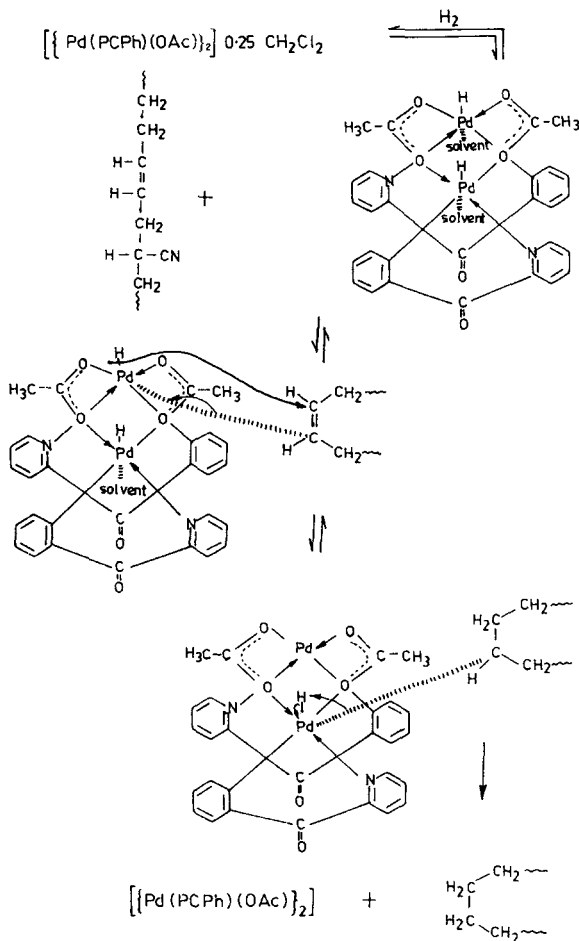
Scheme A.

One of the authors (SB) is thankful to CSIR, New Delhi for providing fellowship to carry out the work.

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