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Aqueous-phase catalytic hydrogenation of unsaturated polymers

Hui Wang, Garry L. Rempel*

Advanced Rubber Technology Lab, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

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ABSTRACT

Unsaturated polymers are a broad group of synthetic and natural polymers that have numerous important commercial applications. The chemical modification of unsaturated polymers via catalytic hydrogenation has led to a number of high-performance elastomers (speciality high-priced products). Recently, considerable attention has grown on carrying out the catalytic hydrogenation in the green aqueous phase to meet the global expectations for green chemistry and chemical sustainability. Herein an overview is provided which focuses on the recent advances toward the development of green and economical catalyst systems and process technologies for catalytic hydrogenation of unsaturated polymers in aqueous media. A general introduction for the unsaturated polymers is first presented, which is then followed by the basic chemistry and general features of the latex hydrogenation process. This article reviews the various types of catalyst systems and technology processes for realization of latex hydrogenation of polymers.

1. General introduction of diene rubbers

Unsaturated polymers used in hydrogenation reactions are macromolecular hydrocarbons with varying degrees of saturation of carbon–carbon double bonds (olefin groups) in the polymer chains of differing polarities and properties as a result of the substituent side functional groups. Because these polymers contain butadiene units that are capable of undergoing further postpolymerization and show rubber-elastic properties at room temperature, they are often referred to as diene-based rubbers from both a commercial and academic sense. Up to the present time, diene-based rubbers and their hydrogenated products are the most important and most widely used rubbers in the modern rubber industry within the rubber family with a variety of more than 20 members (Table 1) [1]. The diene-based rubber group chiefly includes natural rubber (NR), styrene–butadiene rubber (SBR), acrylonitrile–butadiene rubber (NBR), butadiene rubbers (BR), chloroprene rubber (CR), isobutene–isoprene rubber (IIR, butyl rubber), and isoprene rubber (IR, synthetic) as well as their structural derivatives such as halobutyl rubber (brominated IIR and chlorinated IIR), block copolymer of styrene and butadiene (YSBR), block copolymer of styrene and isoprene (YSIR), carboxylated acrylonitrile–butadiene rubber (XNBR), and carboxylated styrene–butadiene rubber (XSBR) [2].

Hydrogenation is an important technique since it not only leads to significant improvements in the chemical, physical, mechanical and thermal properties of the diene-based rubbers but also can be used to obtain polymers that are difficult or costly to synthesize by normal polymerization techniques; for example hydrogenated nitrile butadiene rubber (HNBR). The produced hydrogenated diene rubbers have been found in an ever-growing number of applications which require rubbers with excellent resistance to thermal and oxidative degradation, chemicals, and swelling caused by fuels and mineral oils. As illustrated in the rubber section of Ullmann's Encyclopedia of Industrial Chemistry, completely hydrogenated rubbers are defined as those in which the degree of hydrogenation reaches 99 mol%. Partially hydrogenated rubbers have a degree of hydrogenation of less than 99% while those with a degree of hydrogenation between 90 and 98 mol% are of particular technological interest since they can be vulcanized using traditional sulfur systems [3]. The completely hydrogenated product can be vulcanized (cross-linked) by using peroxides or high-energy radiation. Generally, the sulfur cure gives better physical properties (i.e., higher elongation at break) compared to those obtained after a peroxide cure.

A note of interest that can be addressed here is the difference between the terms rubber and elastomers since both of them are usually used interchangeably. Simply speaking, rubber is the precursor for the production of an elastomer. Rubber is the rubber-elastic polymer at ambient temperature without the processing of vulcanization (cross-linking). Elastomers are polymeric materials that are cross-linked (vulcanized) up to their decomposition points starting from the raw rubber materials. The cross-linking of the C=C

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* Corresponding author. Tel.: +1 519 8884567x32702; fax: +1 519 7464979.
E-mail addresses: h54wang@uwaterloo.ca (H. Wang), grempel@uwaterloo.ca (G.L. Rempel).

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Table 1
Category of rubbers in the chronological order of appearance.

Name of rubber	Abbreviation	Year of appearance	Note
Natural rubber	NR	–	Extracted from *Hevea brasiliensis* rubber trees
Polyisoprene	IR	1887	First synthetic rubber
Styrene butadiene rubber	SBR	1929	Most widely used synthetic rubber
Nitrile butadiene rubber	NBR	1930	First oil resistant rubber
Butadiene rubbers	BR	1950s	Lithium polybutadiene rubber
Polyurethane rubber	PU	1937	
Silicone rubber	SQ	1942	
Butyl rubber	IIR	1943	
Fluororubber	FPM	1948	
Acrylate rubber	ACM	1949	
Chlorosulfonated polyethylene	CSM	1953	
Ethylene propylene rubber	EPM	1959	Ziegler–Natta catalysts
Ethylene vinyl acetate rubber	EVM	1961	
Styrene-*b*-butadiene-*b*-styrene block copolymers	SBS	1962	First thermoplastic elastomers
Epichlorohydrin rubber	CO	1965	
Thermoplastic polyurethane rubber	TPU	1970	
Thermoplastic copolyesters	TPEE	1973	
Polynorbornene rubber	PNR	1975	
Hydrogenated nitrile butadiene rubber	HNBR	1975	Excellent dynamic performance combined with good heat and oil resistance
Acrylate-ethylene rubber	AEM	1978	
Ethylene-propylene rubber	EPM	1979	Thermoplastic elastomers based on cross-linking
Polytetrafluoroethylene-polyolefin blends	–	1981	
Chloropolyolefin	–	1985	Amorphous thermoplastic elastomers
Fluoroalkoxyphosphazene rubber	FZ	1985	Very high resistance to heat and chemicals

located in the polymer chains gives another route that significantly improves the physical properties of rubbers besides the hydrogenation method. A combination of a sufficient degree of cross-linking and high polymer content will improve the dynamic stiffness of elastomers without compromising the physical properties.

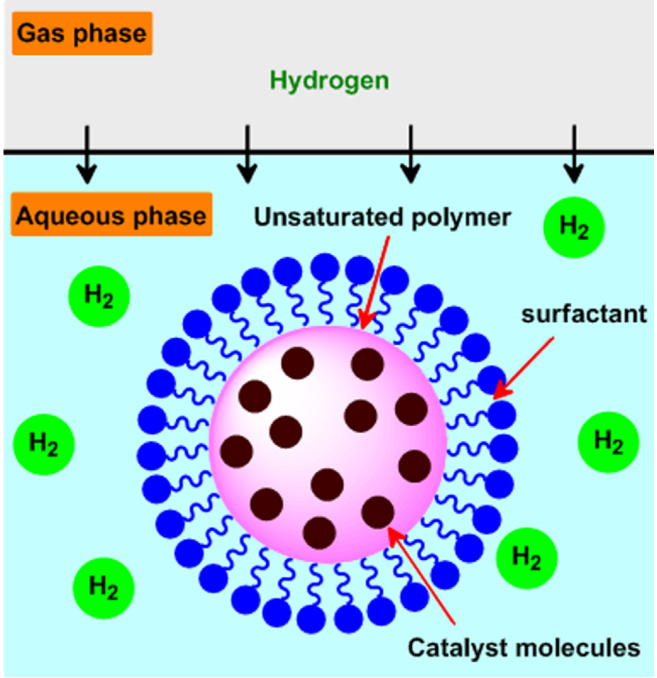
2. Latex (aqueous-phase) hydrogenation

Latex refers generically to a stable dispersion of small polymer particles in an aqueous medium. Rubber latexes may be natural such as NR or synthetic including NBR, SBR, BR, IR, IIR, CR, EVM, ACM, and FPM. Latex products are used extensively as alternatives to organic solvent based systems to produce adhesives, sealants and coatings because of the concerns over environmental pollution and toxicity of solvents as well as for practical reasons, such as ease of use.

Latex hydrogenation is a postpolymerization “green” process to directly hydrogenate the unsaturated polymer particles in a stable dispersion (emulsion) preferably in an aqueous medium (Scheme 1). After hydrogenation, the hydrogenated products such as HNBR become the so-called high performance rubber, which are more resistant than their “parent” polymers toward oxidative and thermal degradation while maintaining their elastomeric properties in chemically aggressive environments [4–7]. Ascribed to these improved superior physicochemical properties, various types of hydrogenated rubbers have found numerous important uses in the automotive, oil-well, aerospace industries and a great variety of performance-demanding applications such as latex film formation coatings.

The current commercial process for the hydrogenation of diene rubbers such as NBR, NR, IR, SBR, BR, etc. is a solution hydrogenation process, which typically involves the following procedures: (1) isolation and purification of the rubber from its parent latex if the rubber was synthesized via emulsion polymerization; (2) dissolution of solid rubber into a sufficient amount of suitable organic solvent to form a solution; (3) hydrogenation under a certain temperature and hydrogen pressure with a catalyst system; (4) recovery of the catalyst and organic solvent after the completion of the hydrogenation. The drawbacks of this solution process are that it has greatly raised environmental concerns and increases the cost of production compared to latex hydrogenation.

In order to avoid the tedious dissolution and separation steps involved in solution hydrogenation and particularly to curb the use of undesirable organic solvents and minimize chemical waste, the hydrogenation of unsaturated polymers in the latex or bulk form is thereby becoming more important and has developed very fast; especially for latex during the past years. Latex hydrogenation has appreciable advantages compared to the solution hydrogenation, since it involves not only an environmentally benign process, but also an energy efficient process. Furthermore, it will be highly attractive when the hydrogenated latex product is the demanded end-use product, such as film formation, coating, and painting applications or only surface/gradient hydrogenation of a product is required. In addition, the direct hydrogenation operation can be



Scheme 1. Illustrative diagram of three-phase latex hydrogenation of unsaturated polymer (© 2012 Wiley) [4].