Hydrogenation of Nitrile Butadiene Rubber: Innovation of the Current Commercial Technology

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Introduction

The hydrogenation of the carbon-carbon double bonds in nitrile butadiene rubber (NBR) is an important process as the hydrogenated NBR (HNBR) is more resistant than NBR towards oxidative and thermal degradation while maintaining its elastomeric properties in chemically aggressive environments[1]. HNBR has been extensively used for automobile components and oil drilling devices. The commercial process for HNBR production involves a number of cumbersome steps, including purifying NBR from the latex, dissolving the NBR in a large amount of organic solvent, and recovering the organic solvent after the hydrogenation operation. It is very desirable to directly hydrogenate NBR in latex/bulk form, as such a process would eliminate the need of a large amount of organic solvent and minimize the negative impact on the environment, which is especially important when HNBR in latex form is the desired end-use product or only the surface/gradient hydrogenation of a product is required. However, while considerable efforts have been made, there has not as yet been realized such a successful process in which a conversion higher than 95 % without crosslinking was achieved (95 % conversion without crosslinking in the resultant HNBR is a threshold to ensure the high performance and the excellent processibility of the product). This presentation reports on our new approaches for successful organic solvent-free NBR hydrogenation.

Materials and Methods

The commercial NBR latex/bulk was provided by LANXESS Inc. H_2 and N_2 were O_2-free being of ultra high 99.999% purity provided by Praxair Inc. Triphenylphosphine(TPP) was recrystallized from ethanol before use. $RhCl(PPh_3)_3$ was prepared according to the synthetic procedure of Osborn and Ahmad et al.[2]. The direct hydrogenation of NBR in latex was carried out in a 300 ml Parr reactor. A measured volume of NBR latex (or with a certain amount of additional water) and TPP were added into the reactor, and then the reactor was sealed. After the mixture was degassed and heated to a designated temperature via a required procedure, the catalyst as solid powder was pressurized into the reaction system by high pressure hydrogen gas. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to discharge the final product and clean the reactor.

Results and Discussion

In order to achieve the direct NBR hydrogenation in latex/bulk form with a high conversion without crosslinking, the key issue is to understand the bottleneck along the hydrogenation path and to find ways to efficiently overcome the bottleneck. NBR hydrogenation in latex/bulk form involves the mass transfer of hydrogen among three/two phases, the dispersion/diffusion of the catalyst, and the hydrogenation reaction as well as the possible side reactions. Via detailed analysis, it is understood that the bottlenecks in both latex and bulk hydrogenation are located in the catalyst dispersion/diffusion as well as the suppression of any possible side reactions. The side reactions are competitive with the hydrogenation reaction. If the hydrogenation reaction is carried out efficiently, the side reactions can be suppressed, i.e., the crucial bottleneck is how to enhance the catalyst diffusion while no alien solvent is used. A novel technical route was so designed that the co-catalyst (triphenylphosphine) could help deliver the principal catalyst (Wilkinson's catalyst) into NBR. Extensive experimental investigation has been carried out with respect to the effects of the ratio of catalyst/NBR, reaction temperature (130-170 °C), hydrogen pressure (250-1000 psi), agitation speed (400-1000 rpm) (latex), and NBR content (2-15 wt%) (latex) on the hydrogenation kinetic performance. It is confirmed that such a designed technical route significantly enhanced the catalyst diffusion and at the same time increased the catalysis efficiency, and the hydrogenation is completely selective towards the C=C. The results show that the degree of hydrogenation of NBR latex/bulk can be higher than 95 % under suitable experimental conditions, and the resultant HNBR contains no visible gel and that the particle size after the hydrogenation was almost the same as it was before the hydrogenation. As an example, Figure 1 demonstrates some of the experimental results and the details will be presented at the conference.

Significance

This is the first time to realize direct hydrogenation of the NBR in latex and in bulk form with a conversion higher than 95 % without crosslinking in the resultant hydrogenated product, which implies that the presence of organic solvent associated with the conventional hydrogenation processes can be significantly greened by eliminating the use of such a large amount of the organic solvent and that pretreatment and post-treatment operations can be significantly simplified.

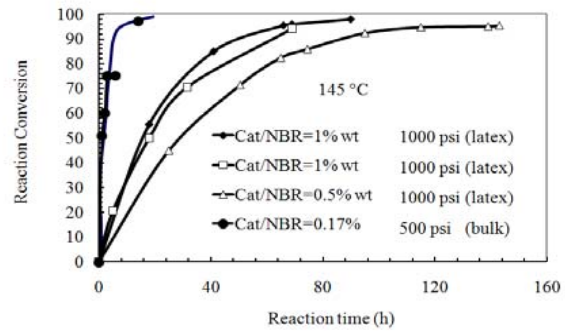

Figure 1. Direct hydrogenation of NBR in latex or bulk form catalyzed by $RhCl(PPh_3)_3$

References

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