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NATURAL RUBBER/ HYDROGENATION/ EPOXIDATIONKANOKTIP BOONKERD : CHEMICAL MODIFICATIONS
OF BUTADIENE RUBBER AND NATURAL RUBBER BY REACTIVE
PROCESSING. THESIS ADVISORS : KRISDA SUCHIVA, Ph.D., PRANEE
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Reactive processing of a polymer is a solventless method of performing a chemical reaction on a polymer while simultaneously physically shaping it in the processing equipment. Because the use of solvents typically limits reaction conditions and imposes costs, the present chemistry is increasingly shifting downstream to reactive processing. In the present study, two reactions, hydrogenation and epoxidation by reactive processing of butadiene rubber (BR) and natural rubber (NR), were studied. Experimental procedures for carrying out the reactions were established. For hydrogenation performed by a noncatalytic method using p-toluenesulphonyl hydrazide (TSH) as a hydrogenating agent, two steps composing premixing of the rubber with TSH followed by hydrogenation in compression mould proved to be suitable. The effects of the reaction temperature, reaction time and mole ratio of TSH to double bond, $[TSH]/[C=C]$, on the percentage of hydrogenation were studied.

The percentages of hydrogenation of solid BR attained were relatively low, i.e., 16-36% depending on the $[TSH]/[C=C]$ ratio. Increasing the reaction temperature and reaction time resulted in increases of the percentage of hydrogenation. The increases were between 1 and 20% depending on the $[TSH]/[C=C]$ ratio involved. Limited solubility of TSH in BR was believed to be the major factor responsible for the attainment of relatively low percentage of hydrogenation of BR. However, for the same $[TSH]/[C=C]$ ratio, hydrogenation of BR by reactive processing gave higher percentage of hydrogenation than that of the reaction carried out in solution. For NR, the highest percentages of hydrogenation attained were 20% and 34%, depending on whether the nominal $[TSH]/[C=C]$ ratios of 1:2 and 1:1 were used, respectively. Solution hydrogenation of NR also gave much lower percentages of hydrogenation. Cis-trans isomerisation was also observed in the hydrogenation of both BR and NR. The thermal stability of hydrogenated BR was distinctly improved over that of unhydrogenated counterpart but the improvement for NR was less certain.

Epoxidation of solid NR in the internal mixer using m-chloroperbenzoic acid (m-CPBA) proved to be unsuccessful. Only low percentages of epoxidation (1-10%) were obtained despite varying the reaction time and the $[TSH]/[C=C]$ ratio. The difficulty in lowering and maintaining the temperature of the reaction mixture at low levels required for efficient epoxidation while in the mixer was believed to be the reason for the poor results.