



Optimizing the usability of unwanted latex yield by *in situ* depolymerization and functionalization



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ABSTRACT

Functionalized liquid natural rubber (FLNR) derived from unwanted latex yield was synthesized by redox method using hydrogen peroxide (H_2O_2) in the presence of sodium nitrite ($NaNO_2$). Hydroxylation was confirmed by FTIR with a peak at 3424 cm^{-1} . Response surface methodology was used to investigate the effect of varying feed parameters towards response of molecular weights and OH values. Response surface contours were constructed for modeling the relationship between processing factors and response output. The developed models show $NaNO_2$ as the main factor followed by H_2O_2 that influences the FLNR properties. Multi response optimization was done using Derringer's desirability function. The optimum conditions for minimizing M_n and MWD while maximizing OH value was determined to be at low ratios of $NaNO_2/H_2O_2$ and high ratios of H_2O_2 /isoprene unit. The predicted optimum response for M_n was around 30,000 g/mol, MWD between 1.48 and 1.61 and OH value between 194 and 229 mg KOH/g.

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1. Introduction

The Pará rubber tree, *Hevea brasiliensis*, is a major commercial source of natural rubber (NR) that has been extensively used to manufacture high quality rubber products (She et al., 2013). In recent years, most products from NR have focused on tires, gloves, liners, catheters and the tube industry. Since NR is a renewable source, it has become of particular interest for ongoing research to develop and refine its processing techniques to produce greater product varieties for development of this industry. As a starting material, NR has a hydrocarbon structure that can be modified further to diversify its applications. Among the many derivatives of NR products is its depolymerization into functionalized liquid natural rubber (FLNR). These derivatives with low molecular weight ($M_n \leq 30,000$) are gaining high potential uses as new development products especially for thermoplastic rubber purposes (Abdullah and Ahmad, 1992; Cenens and Hernandez, 1999; Dirckx et al., 1999). The commercialization of FLNR and its first production on a small scale basis was done as early as 1923. The simplest method for the preparation of FLNR involves the oxidative chain scission of the polyisoprene backbone (Ravindran et al., 1986). The chemical depolymerization of NR is a straightforward method of creating FLNR that can be used for additives such as compatibilizer (Ahmad

et al., 1994; Dahlan et al., 2000; Mounir et al., 2004), adhesive (Dileep et al., 2003), coating (Phinyocheep and Duangthong, 2000; Wood, 1990), thermoset polyurethane (Cavallaro et al., 1997), and interpenetrating polymer networks (IPN) (Glennon, 1981, 1982; Tanaka et al., 1999). The modification of FLNR with hydroxyl groups would have many advantages. These prepolymers are capable of entering into further polymerization or other reactions through its reactive groups which can improve its physical and mechanical properties. The various chain extension reactions can also result in higher value end products with new tailored properties for other specific applications (Brosse et al., 2000). The production of thermoplastic polyurethane (TPU) based on natural rubber (NR) modification is a good alternative to shift away from the dependence on petroleum based materials which it is normally sourced from.

However, one of the major factors impeding the use of FLNR obtained from depolymerized liquid NR is its high cost. While the average cost of NR from 1990 to 2015 was estimated at \$0.63 USD per pound (Malaysian Rubber Board, 2015), depolymerized liquid NR has steadily increased from \$3.50 to \$4.00 USD per pound from 2011 to 2015 (DPR Industries, 2015). Currently, the world natural rubber production is forecast to rise 4.3 percent annually to around 12 million tons per year (Fainleib et al., 2013); a certain amount of it is discarded in the producing countries during working operations (coagulation, washing, sheeting, etc.). These rejects could be a valuable source of depolymerized liquid NR, at a reasonable cost

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in comparison with petroleum-based isoprene derivatives, because in this case the cost of the starting substrate is practically zero.

Previous research on FLNR have mostly focused on concentrated latex, rubber sheet, crepe rubber and crumb rubber from field latex but in this study the raw material used is sourced from the unwanted portions of the latex tapping yield (low quality cup lump). It is rarely used for high quality rubber-based products and normally discarded as waste because of its low purity and high molecular weight. This otherwise wasted leftover latex yield was selected because of its attractively low cost and ease of treatment for the reaction as well as having cleaner, more uniform and better aesthetic properties after processing compared to recycled rubber.

Commonly, multi-step processes have been used to produce FLNR. In the current work, we will use the redox method (Gillier-Ritoit et al., 2003; Gupta et al., 1985; Isa et al., 2007) to simultaneously depolymerize and functionalize NR into FLNR and in a later work, will be used as a precursor for producing semi-rigid TPU. Previous researchers (Brosse et al., 1981) have reported a redox method for the depolymerization of NR chain using a phenylhydrazine/O₂ couple system. The intensity and extent of the chain scission reaction depended upon temperature, reaction time and concentration of the reducing agent. By depolymerizing NR into shorter chain segments, it was possible to obtain FLNR with useful and interesting technological applications (Bac et al., 1993). The possibility of hydroxylation have been pointed out previously by using perphthalic acid (Brosse et al., 1981) or by *in situ* methods (Gazeley and Mente, 1987).

Despite the above mentioned works, few detailed studies have been made on the influence of the chain scission reaction on the hydroxylation process and on the structure of the final product. Hydrogen peroxide is an effective agent to break down the molecular chain and provides OH functionality on the polymer backbone of the NR (Ravindran et al., 1986; Wang et al., 2009). However, at high temperatures, hydrogen peroxide is unstable and will also form side reactions such as furanization and crosslinking (Zhang et al., 2010). NR that was heated up to 150 °C at a pressure of 200–300 psi had been reported to yield FLNR having M_n between 2500 and 3000 g/mol with low efficiency of functionalization of the NR due to side reactions (Gupta et al., 1985). To mitigate this effect, several other researchers have introduced sodium nitrite to the reaction mix (Bac et al., 1993; Gazeley and Mente, 1987). This type of chain scission could be applied for hydroxylation of NR, leading to a more efficient reduction of molecular weight as well as avoiding crosslinking side products.

For our application, the molecular weight of the FLNR must be low and it must be highly functionalized with hydroxyl groups. Prior art (Cenens and Hernandez, 1999; Dirckx et al., 1999) have reported that the suitable molecular weight required of FLNR to produce TPU should be about 25,000 g/mol and the best is less than 10,000 g/mol. Tailoring of the end-product properties of TPU is dependent on the OH value. It has been reported that the formulation of flexible polyurethane contains OH value of less than 100 mg KOH/g, semi-rigid polyurethane is between 100 and 300 mg KOH/g and rigid polyurethane is between 200 and 1500 mg KOH/g. Thus, knowledge of parameter control (variables) in the synthesis procedures is critical to achieve the desired molecular weight and OH value.

In general, the step-wise experimental study approach for each of the parameters involved in the synthesis procedures is not only time consuming but also requires special attention in cases where there is a contribution of multiple parameters interacting simultaneously in the system. Therefore, an appropriate model can be of significant interest to simulate and predict the responses from the parameters involved in the synthesis process. Among the modeling approaches, the response surface methodology (RSM) is a powerful technique in optimizing the industrial process. RSM is

recognized as a simple and reliable tool for a multivariable system. It can effectively analyze the effects of several independent variables simultaneously without any knowledge on the relationship between the objective functions and variables (Aimi et al., 2014; Sinha et al., 2013; Sun et al., 2011). RSM can be very helpful in designing the experiments and to elucidate the correlations among the many variables of any industrial process. It is then used to build the relationship between the input parameters and output response using fitness functions to measure fitness values by numerical approaches. The RSM uses the analysis of variance (ANOVA) to determine which parameters have the strongest interactions and/or which ones exhibit significant influence on the outputs of the process. The process responses are then represented as statistical developed models. The technique can model the response in terms of all parameters, their interactions and square terms. Finally, the RSM analysis can be used to predict the optimum conditions required for the parameter combination to yield responses from a set objective (Derringer and Suich, 1980; Martinez Delfa et al., 2009).

As mentioned above, experimental designs focusing on reaction time, temperature, or other variables have already been extensively studied. However, studies on the relationship of molar ratios of H₂O₂ and NaNO₂ as the reagents have been scarce until recently (Ibrahim and Mustafa, 2014). Although they have made significant characterization of their experimental responses using GPC, NMR, and FTIR, and also identified a single optimum point with it, a statistical model describing the relationship between the molar ratios of the two reagents was not clearly elucidated. In this study, the simultaneous depolymerization and hydroxylation of NR was done *in situ* using a NaNO₂/H₂O₂ system. The aim of the present work is to study the effect of varying the amounts of H₂O₂ and NaNO₂ in the reaction feed towards the resulting properties of molecular weight and formation of hydroxyl functionality of the synthesized FLNR. RSM is used for studying these variables for the depolymerization and hydroxylation process to predict the outcome of the molecular weight and OH content of FLNR.

2. Experimental

2.1. Materials

The NR sample ($M_n = 1.207 \times 10^6$ g/mol, PDI = 4.26) was supplied from the Felda Lurah Rubber Factory, Bilut, Pahang, Malaysia. All other reagents were supplied from Merck and are of analytical grade. The following are materials that were prepared and used in this work: 30% hydrogen peroxide (H₂O₂), 30% aqueous absolute ethanol, sodium nitrite (NaNO₂) solution (10% w/v in aqueous absolute ethanol), hydroquinone, toluene, and tetrahydrofuran (THF) for gel permeation chromatography (GPC) measurement.

2.2. Preparation of functionalized liquid natural rubber

All experiments were performed using laboratory scale conditions. Initial pilot runs with purified and unpurified cup lump material showed no significant difference in the final properties, indicating that the processing method is robust. Hence, for the rest of the experimental design the cup lump material was used as received without further purification. Solid NR in cup lump form was dissolved in toluene (1% rubber solution in 800 ml toluene) overnight at room temperature with stirring. The obtained homogenous NR solution was then heated to 60 ± 1 °C within 30 min to 1 h. H₂O₂ solution was then added dropwise to the NR solution and allowed to stir for 20 min. Then, alcoholic sodium nitrite solution was added dropwise and allowed to stir for another 30 min. The reaction mixture was then heated to 90 ± 1 °C within

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