

EFFECT OF FILLER-CURING AGENT INTERACTION ON THE VULCANIZATION RATE OF STARCH/SBR COMPOSITES

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1 Introduction

Recently, with the aggravation of pollutions and the depletion of energy, green composites have received increasing attention due to their renewability and biodegradability. Among lots of renewable resources, starch is an abundant and very cheap resource. Therefore, more and more scientists focused on starch-based composites.

The application of starch as elastomer filler was firstly reported by Buchanan, who prepared zinc starch xanthate/SBR composites by a co-precipitation process [1]. In 1997, Goodyear Tire & Rubber Company research group found that addition of starch would reduce the rolling resistance of tire [2, 3]. This lower rolling resistant tire was called BioTRED. In recent year, high-performance starch/rubber composites were successfully prepared by several groups [4-6]. They indicated that small particle size, well dispersion and strong interfacial interaction are advantageous for high-performance starch/rubber composites. Most of earlier research concentrated on the reinforcing mechanism of starch. There is little report about the cure characteristic of starch/rubber composites. Lorenz and Parks indicated a filler-curing agent interaction might influence the rate of crosslinking and gave rise in filled stocks to vulcanization rates different from those in gum stocks [7]. Therefore, starch-curing agent interaction might take place and affected the vulcanization rate of starch/rubber composites.

In this present study, two types of starch: pure starch modified starch (M-starch) were blended with SBR on a two-roll miller. M-starch was synthesized by grafting of methyl methacrylate monomer using ceric ammonium nitrate-initiated radical polymerization. Coupling agent styrene-g-(maleic anhydride) (SMA) was used to improve the starch-SBR interaction and decrease the starch-curing agent interaction. The effect of starch – curing agent interaction on the cure characteristics of composites was investigated.

2 Experimental

2.1 Materials and sample preparation

SBR Latex (SBR 1502) was purchased from KumHo Rubber Company, South Korea. Corn starch was purchased by Samyang Genex Company, South Korea. Coupling agent styrene-co-maleic anhydride (SMA) (MA content: 32%) was purchased from SIGMA-ALDRICH Company. Methyl methacrylate monomer and initiator ceric ammonium nitride were purchased from Dae Jung Chemical and Metal co., Ltd.

2.2 Sample preparation and characterization

M-starch was synthesized by grafting of methyl methacrylate monomer. Grafting copolymerization was carried out in an aqueous medium using ceric ammonium nitrate (CAN) as initiator under nitrogen atmosphere according to literature [8]. Compounding was carried out on a two roll mill at 50-60 °C. The formulations were listed as follow: SBR 100phr, starch or M-starch 20phr, coupling agent SMA 0, 1, 3, or 5 phr, sulfur 2 phr; stearic acid 1 phr; zinc oxide 3 phr; accelerator CBS 2 phr; accelerator MBTS 0.5 phr; antioxidant TMQ 1 phr. Starch/SBR and M-starch/SBR composites with 0, 1, 3, 5 phr content of SMA were prepared.

Curing characteristics were measured according to ASTM D2084 on a moving-die rheometer (MDR) 2020 reometer at 140, 150, 160°C. Some cure parameters, such as minimum torque S_{min} , maximum torque S_{max} , scorch time t_{S2} , and cure time t_{90} could be derived from the cure curve.

3 Result and discussion

The curing curves of starch/SBR and M-starch/SBR at 140, 150, and 150°C with 0, 1, 3, 5 phr SMA were shown in Figure 1, 2, 3 and 4, respectively.

It was clear that increasing of temperature led to decrease the minimum torque S_{min} and maximum torque S_{max} . It may be attributed to the breakdown of

sulfur crosslinking at higher temperature. Costa et al. suggested that at higher temperature sulfur crosslinking were more susceptible to breakage giving rise to intra-molecular sulfur cyclization and no longer contributing to the network formation [9]. It was also observed that at same temperature and SMA content, both S_{\min} and S_{\max} of M-starch/SBR composites were higher than those of starch/SBR composites. M-starch/SBR composites showed longer scorch time t_{s2} and curing time t_{90} compared to starch/SBR composites. Moreover, scorch time t_{s2} and curing time t_{90} increased as increasing of SMA content in both starch/SBR and M-starch/SBR composites.

An assumption that the vulcanization process followed first-order kinetics was applied to calculate the vulcanization rate. The kinetic equation for vulcanization process was given as follow [10]:

$$\ln\left(\frac{M_h - M_l}{M_h - M_t}\right) = kt \quad (1)$$

M_h , M_l , and M_t represented the maximum torque, minimum torque and torque at a given time t , respectively. K is the vulcanization rate constant. Since the rate in the first stage reflected the character of the main forward reaction, M_t values from 25% to 45% of value changes were chosen to estimate the rate constant k [10]. After rearrangement of equation (3), the equation (4) was obtained:

$$\ln(M_h - M_t) = \ln(M_h - M_l) - kt \quad (2)$$

By plotting $\ln(M_h - M_t)$ against the time t , a straight line graph was obtained as shown in Figure 5. Therefore, it confirmed that the vulcanization reaction followed the first-order kinetics. The vulcanization rate k could be obtained from the slope of the line as shown in Figure 6.

It was observed that at the same temperature, the vulcanization rate k of starch/SBR compounds was always greater than that of M-starch/SBR compounds and decreased successively with increasing of SMA content. These observations showed well agreement with the results of scorch time t_{s2} and curing time t_{90} . These phenomena could be interpreted by the occurrence of filler-curing agent interaction.

It is well known that starch contain many hydroxyl groups on their backbone. These hydroxyl groups were easily form hydrogen bond with amine or sulfur groups of accelerator CBS. The formation of starch-CBS interaction led to weaken the bond strength of N-S of CBS and enhance the breakdown ability of N-S bond. Therefore, starch accelerated

vulcanization rate due to enhance the dissociation ability of N-S bond by strong starch/CBS interaction. However, after starch was modified by grafting of methyl methacrylate monomer, the hydroxyl groups decreased, resulting in decreasing starch-CBS interaction. The ability of breakdown N-S bond also decreased. Therefore, the vulcanization rate decreased. With addition of coupling agent SMA, the hydroxyl groups further decreased due to the esterification between SMA and starch or M-starch, which resulted in the lowest starch-CBS interaction. Therefore, M-starch/SBR composites with 5phr SMA exhibited the slowest vulcanization rate. Overall, we concluded that in starch/SBR and M-starch/SBR composites, the starch-CBS interaction truly occurred due to the formation of hydrogen bond. The vulcanization rate was closely related to starch-CBS interaction. By tailoring the number of hydroxyl groups in starch backbone, we could obtain the desirable vulcanization rate.

Moreover, at higher temperature (160°C), the difference in vulcanization rate k between starch/SBR and M-starch/SBR compounds was much greater than lower temperature (140°C). For example, when concentration of SMA was 0, the difference in vulcanization rate k between starch/SBR and M-starch/SBR compounds was 0.51 min⁻¹ at 160°C, whereas at 140°C, the difference was 0.08 min⁻¹. Also, it was observed that at higher temperature, the effect of SMA content on the cure rate constant k was more significant compared to lower temperature. All of these phenomena were due to sufficient thermal energy being available at higher temperature to overcome the activation energy of vulcanization [11].

4 Conclusions

Starch/SBR and M-starch SBR composites were prepared by solid blending method. Cure characteristics were investigated. Result showed M-starch/SBR composites exhibited slower vulcanization rate compared to starch/SBR composites. Coupling gent SMA further decreased the vulcanization rate. These phenomena were attributed to the weakening of starch-CBS interaction. Modification of starch could reduce the starch-CBS interaction and improve the efficiency of accelerator CBS. These observations have guiding significance for the vulcanization process of starch/rubber composites.

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List of Figure

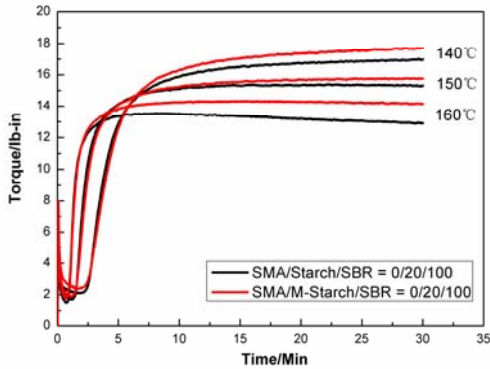


Figure 1. Rheographs of starch/SBR and M-starch/SBR composites with 0 phr SMA.

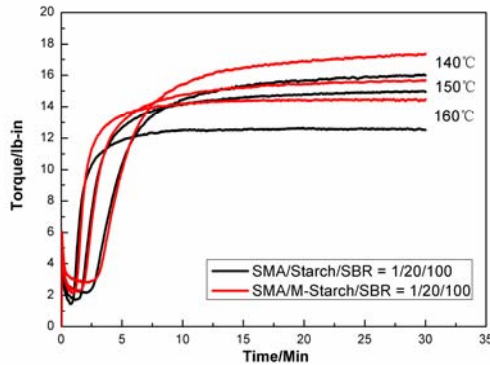


Figure 2. Rheographs of starch/SBR and M-starch/SBR composites with 1 phr SMA.

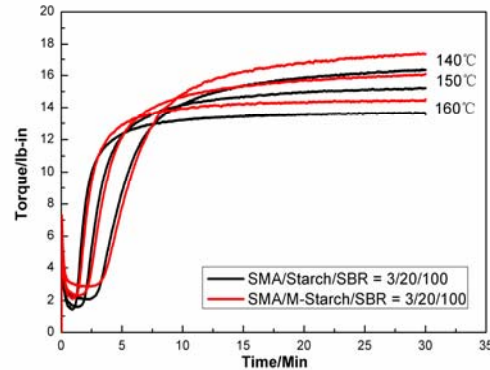


Figure 3. Rheographs of starch/SBR and M-starch/SBR composites with 3 phr SMA.

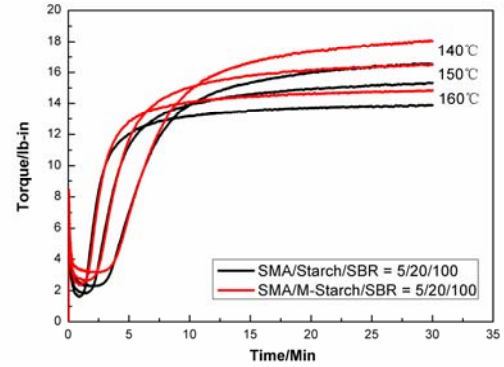


Figure 4. Rheographs of starch/SBR and M-starch/SBR composites with 5 phr SMA.

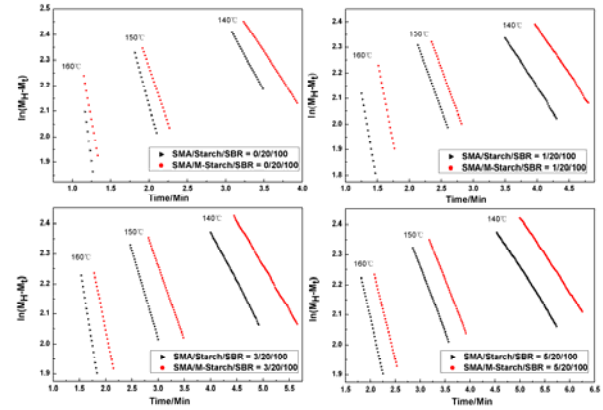


Figure 5. Plots of $\ln(M_h - M_t)$ vs. vulcanization time t at different temperature.

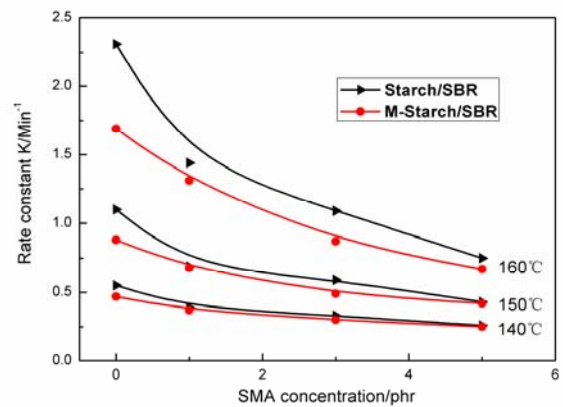


Figure 6. Vulcanization rate K of rubber composites with different concentration of SMA at 140, 150 and 160°C.

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