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Investigation of cure and mechanical properties of deproteinized natural rubber-g-poly methyl methacrylate

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Abstract

Investigation of cure and mechanical properties of graft copolymer of deproteinized natural rubber (DPNR) with methyl methacrylate (MMA) prepared by graft copolymerization in latex was presented in this work. It is determined that the increase in scorch time, cure time, hardness and tear strength of the graft copolymer were depended on monomer concentration. With the monomer concentration of 15 g/100 g rubber, the increase of hardness and tear strength are 68 % and 66 %, respectively, compared to DPNR. Besides, there are increasing trends of tensile strength and elongation at break. The optimum concentration of MMA monomer is found at 15 g/100 g-rubber. At this monomer concentration, the hardness and tear strength of the graft copolymer increased, whereas the elongation at break and the tensile strength decreased a bit compared to the natural rubber.

Keywords. Natural rubber, polymethyl methacrylate, grafted copolymer, curing properties, mechanical properties

1. INTRODUCTION

Natural rubber (NR) is composed of 93-95 % cis-1,4-polyisoprene. It is an unsaturated elastomer having excellent properties, such as high strength, outstanding resilience and high elongation at break [1]. However, NR is very sensitive to heat oxidation due to the presence of double bonds in its molecular structure. These drawbacks have been overcome by some approaches, for example modification of NR by graft copolymerization with a vinyl monomer. Preparation of graft copolymer of DPNR with poly methyl methacrylate (DPNR-g-PMMA) has been one of the main interesting field [1-4]. The graft copolymerization of MMA monomer onto DPNR in latex with redox initiator tert-butyl hydro peroxide/tetraethylenepentamine (TBHPO/TEPA) was investigated in our previous work [3]. In this work, we aim to study the role of MMA in improving the cure and mechanical properties of natural rubber.

2. EXPERIMENTAL

2.1. Materials

2.1.1. The materials for graft copolymerization

High ammonia natural rubber (HANR) latex

containing 60 % dried rubber content (DRC), Merufa company (Vietnam). Sodium dodecyl sulfate (SDS) and urea, Nacalai Tesque (Japan). MMA, TEPA and TBHPO, Sigma Aldrich.

2.1.2. The materials for vulcanization

The sulfur, zinc oxide, stearic acid, accelerators including disulfua mercapthobenzothiazone (DM), mercapthobenzothiazoyole (M) and antioxidant TMQ (RD), China.

2.2. Preparation of samples

Various graft copolymers (DPNR-g-MMA) were prepared according to our previous work [3], that are, DPNR-g-PMMA 5, DPNR-g-PMMA 10, DPNR-g-PMMA 15, DPNR-g-PMMA 20 with the monomer concentrations are 5, 10, 15, 20 wt%, respectively. DPNR samples are also prepared as control samples.

The rubbers are vulcanized according to the formulation in table 1.

The vulcanization was carried out using an internal mixer (Brabender, Germany). Mixing chamber was 60 cm³ and the batch sizes were 50 ± 5g. Mixing was operated at a constant rotor speed at a temperature of 50 °C. The mixing for each batch took place for 13 minutes. Firstly, a rubber sample

was added into the mixing chamber and mixed for 6 minutes, followed by stearic acid, ZnO and RD addition and the mixing for another 4.5 minutes. The sulphur, DM and M were added into the system and it was continued to mix for 2.5 minutes to complete the dynamic vulcanization process. The mixture was immediately removed from the chamber and left at room temperature for 24 hours. Subsequently, the produced rubber was pressed using hot press for about 5 minutes (with DPNR-g-PMMA samples) and 14 minutes (with DPNR sample) at 150 °C and 10 MPa [2, 4, 5].

Table 1: Compounding formulations.

Ingredients	Concentration (phr)
Rubber*	100
Stearic acid	2.5
ZnO	5
RD	1.5
Sulphur	1.7
DM	0.8
M	0.2

*Including DPNR and graft copolymers with different monomer concentration.

Subsequently, the obtained sheet was cooled down under room temperature. The sheet was cut into small samples with a size according to the TCVN and ASTM standard for mechanical testing. The samples were kept at room temperature for 24 hours before testing [2, 4].

2.3. Mechanical testing

The rubber compounds were compression molded into test specimens at 150 °C according to the respective cure times determined by Rheometer RLR-4 (Japan).

Tensile test and tear test were performed by INSTRON 5300 100 KN machine (USA) and carried out according to TCVN 4509:2006 and TCVN 1597-1:2006, respectively. The sample for tensile test was cut using standard "dumbbell" according to JIS K6251. The sample for tear test was cut into the crescent shape [4, 5].

The hardness test was performed using a Shore type durometer TFCLOCKGS 709N equipment (Japan).

All tests were carried out at room temperature.

3. RESULTS AND DISCUSSION

In the present work, the content of PMMA is

proportional to the concentration of MMA as shown in the table 2. This means that the content of PMMA in DPNR-g-PMMA increases when monomer concentration increases.

Table 2: Relationship between MMA concentration and MMA content

MMA concentration (%)	Content of PMMA in DPNR-g-PMMA (%)
5	3,8
10	7.1
15	11.7
20	15.9

3.1. Curing characteristics

The first curing characteristic is scorch time. It is a measurement of the time at which vulcanization starts. The variations of scorch time of DPNR and DPNR-g-PMMA at various concentrations of MMA were shown in figure 1. It is clearly seen that the scorch time decreases with increasing of monomer concentration.

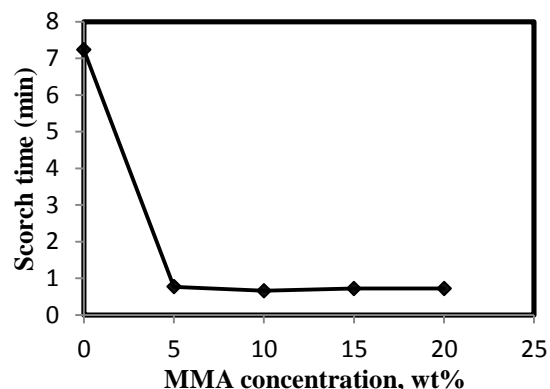


Fig. 1: Scorch time of DPNR-g-PMMA at various concentration of MMA

Moreover, the scorch time of DPNR was 7 times long as those of the DPNR-g-PMMA samples. This observation may be attributed to the higher level of unsaturation in the rubber chain in DPNR compared to that of DPNR-g-PMMA [4]. Increasing the level of the MMA concentration resulted in a slow decreasing trend of the scorch time. This may be due to the influence of PMMA chains between rubber chains on accelerating the time to incipient cure. Therefore, it is concluded that the levels of PMMA chains also played a significant role on accelerating the cross-linking reaction [4].

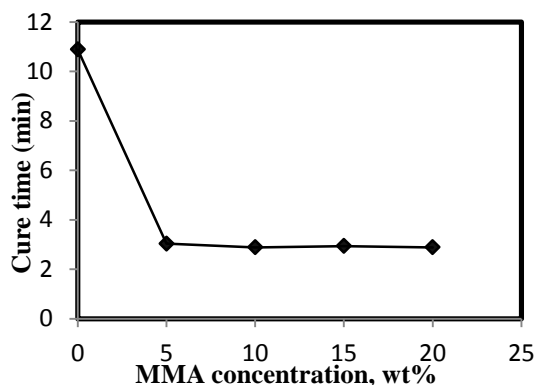


Fig. 2: Cure time of DPNR-g-PMMA at various concentration of MMA

A decreasing trend of the cure time was also observed upon increasing concentration of MMA, as shown in Fig. 2. The cure times of the DPNR-g-PMMA samples were also shorter than that of DPNR sample. Cure rate index is a measure for rate of vulcanization based on the difference between optimum vulcanization and incipient scorch time. The cure rate index is calculated as follows [4]:

$$\text{Cure rate index} = \frac{100}{\text{cure time} - \text{scorch time}}$$

Figure 3 shows the cure rate index of the DPNR and DPNR-g-PMMA at various concentrations of MMA.

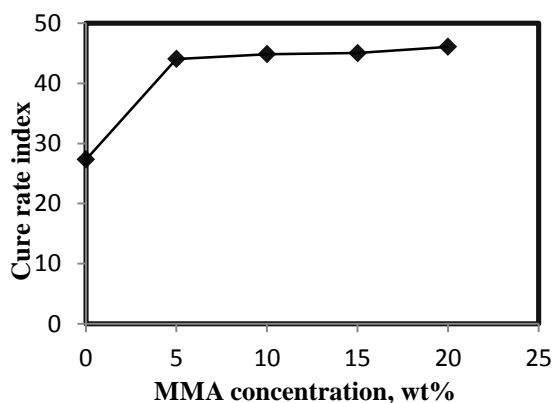


Fig. 3: Cure rate index of DPNR-g-PMMA at various concentration of MMA

Only a slight increase in the rate of vulcanization was observed upon increasing levels of MMA in the DPNR-g-PMMA. However, the abrupt increase in the rate of vulcanization was observed for the DPNR-g-PMMA compared to DPNR. Therefore, increasing levels of the PMMA in the grafted rubber causes the increasing rate of vulcanization. This may be attributed to the acceleration of the cross-linking reaction in the

presence of the PMMA chains. This is because of the increased number of reactive sites on the rubber molecules used for the cross-linking reactions [4].

3.2. Tear strength

Figure 4 shows the tear strength at various concentration of MMA. It can be seen that tear strength increases dramatically in graft copolymer compared to DPNR and gradually increases with an increase in concentration of the MMA. This result may be associated with the ability of PMMA to transfer the tearing force, and also probably because of PMMA grafted onto DPNR chains distributing force more sides [2, 5].

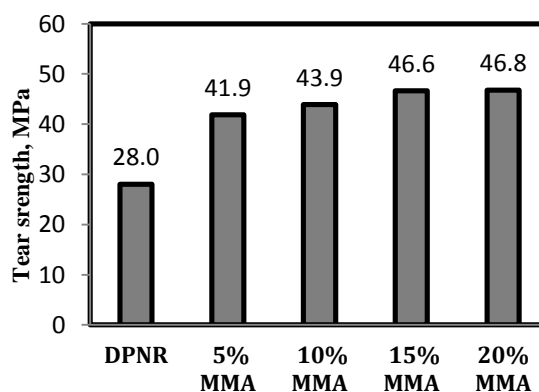


Fig. 4: The tear strength of DPNR-g-PMMA at various concentration of MMA

3.3. Hardness properties

Figure 5 shows the dependence of hardness on MMA concentration. It is shown that the hardness increases as concentration of monomer increases. In other words, the rubber vulcanizes become stiffer and harder as the MMA concentration increases. The stiffness of the vulcanizates is ascribed to be

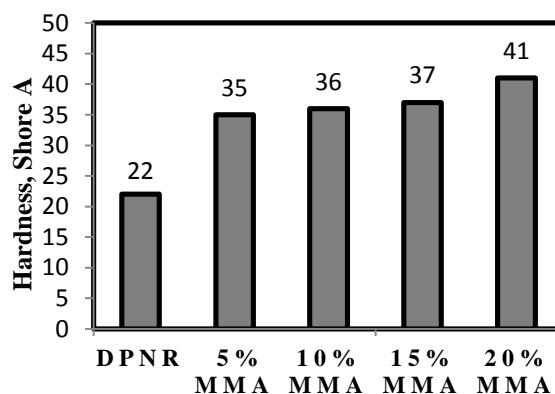


Fig. 5: Hardness of DPNR-g-PMMA at various MMA concentrations

due to the grafted PMMA on rubber molecules. Therefore, the elasticity of the rubber chains is reduced, resulting in more rigid vulcanizates [2, 4].

3.4. Tensile properties

The effect of monomer concentration on the tensile strength of the DPNR-g-PMMA is shown in Fig 6. It was found that the tensile strengths decreased gradually with an increase of MMA concentration. These rather poor strength properties may be attributed to the spatial structure and the concentration of the MMA in the grated rubber. The results obtained are in agreement with the elongation at break (EB) in Fig 7. That is, the EB drops continuously with an increase of the concentration of MMA. This trend may be ascribed to the increase in rigidity of DPNR-g-PMMA when the MMA concentration increases [2, 4, 5]. This behavior is a similar case as particulate filler in the rubber compounds increases. The increment in filler content is found to reduce deformability of an interface between the rigid filler and the rubber matrix [4].

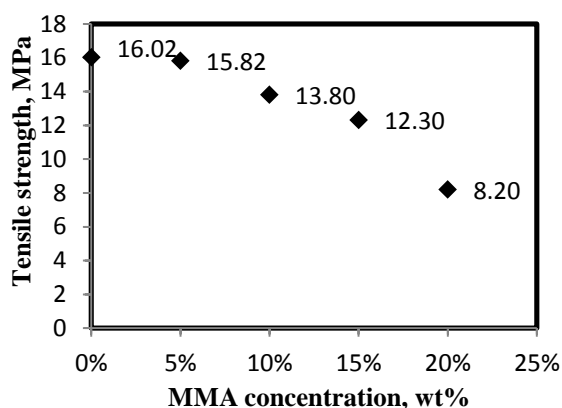


Fig. 6: The tensile strength of NR-g-PMMA at various concentration of MMA

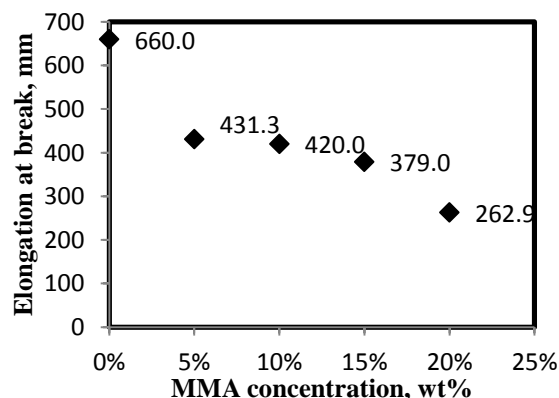


Fig. 7: The elongation at break of DPNR-g-PMMA at various of MMA concentration

4. CONCLUSION

Cure characteristics and mechanical properties, such as tensile strength, ultimate elongation, tear strength and hardness, were quantified. It is found that the scorch time and cure time decreased with increasing concentration of MMA. Also, the scorch time and cure time of DPNR were higher than those of the DPNR-g-PMMA samples. It was concluded that the PMMA chains and degree of unsaturation in the rubber chain might be responsible for the trend of the scorch time and cure time. The cure rate index increased with the increase of MMA concentration. The hardness and tear strength also increased. However, increasing concentration of MMA caused decreasing trends of tensile strength, elongation at break.

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