SYNTHESIS AND CHARACTERIZATION OF ACRYLIC RUBBER

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1 Introduction
In 1970's, Rubber industry had been mainly developed with footwear industry. But as footwear industry had been reduced and automotive industry had been increased, rubber industry has been grown with automotive accessorize (including tire). At 1960’s, Importing tire technology for automotive induced tire exporting market. While demand has been expended, inbound rubber industry also had achieved rapid development. Synthetic rubber market has been changed with the growth speed of automotive market. Rubber parts used for automotive is only 5% of total weight of automotive. But it is mainly used for important part which is main key of automotive performance. Especially synthetic rubber is used as raw material of important part, such as what makes shock/noise and requires heat/oil resistance. Among these several special rubbers, Acrylic rubber has heat/oil resistance and ozone resistance. So it is mainly used for automotive seal and packing. It is known and used as important property for automotive parts. Development of Acrylic rubber has long history, but the usage was not good, because it was very poor to use for processing. Also high price affects poor usage.

Recently, processing technology is getting better so requirement of Acrylic rubber is increased. It is expected to be used widely as the rubber, second to fluorine rubber, which has heat resistance and oil resistance. Even with this popularity, Acrylic rubber's chemical formation has not been known. So in this experiment, we studied the matters that require attention while manufacturing acrylic rubber using several monomer. Also property and transformation of each monomer is studied.

2 Experimental
2.1 Materials
2.1.1 Polymerization
Emulsifier was SDBS (Dodecylbenzensulfonic acid sodium salt 50%, JunSei), Initiator was APS (Ammonium persulfate, Aldrich), Monomer were EA (Ethyl acrylate, SamChun Chemical), MEA (2-methoxyethyl acrylate, Tokyo kasei), BA (Buthyl acrylate, DaeJung Chemical), GMA (glycidyl methacrylate, Aldrich) sovent was DIW (Deionized water)

2.1.2 Compound
Carbonblack (N550, FEF Type, Deajunghwagum), DCP (Dicumyl peroxide, Aldrich), 2,2-dibenzothiazolyl disulfide, Aldrich), stearic acid, TETA (Triethylentetramine, Aldrich), MBTS (2,2-dibenzothiazolyl disulfide, Aldrich), DPG (Diphenyl guanidine, Aldrich) BAPP (2,2-bis[4-(4-aminophenoxy)phenyl]propane, Aldrich).

2.2 Polymerization
Polymerization methods were soap-free emulsion (SDBS mixing EA, BA, MEA, GMA) drop in a 1000ml Pinex with APS during 3 hours, after that spend 1 more hour for aging. Input a small initiator to pinex End of polymerization. respectively experiment recipe were Table 1.

Soap rate were monomer about 1%, monomer, monomer rate were DIW about 70/30%, Initiator rate were monomer about 1% and t-BHPO, SMBS were 0.1%

2.3 Compounding
ACM compunds with a variety of cross-link densities were prepared on a two open roll mill. The ACM was firstly masticated and Carbon black(30phr) on the mill for 20 min. After that, stearic acid(2phr) mixed for ACM sticky, after that, BAPP(1phr) with variety of amounts were added. The mixing times for the
chemicals were 10min, respectively. After mixing for a given time, the rubber sheet was removed to cool down before returning to the mill and further mixed with DCP and TETA for 10min. Respectively experiment recipe were Table 1.

2.4 Vulcanization
Optimum cure time (t90) for each compound was determined by using a Rheometer (MyungJi Tech, M.D.R-2020) operating at 160°C after that, the rubber compounds were vulcanized in a Hot press to the optimum cure time at the same temperature.

2.5 Characterization
2.5.1 FTIR spectroscopy
The FTIR spectrums of Sixteen scans were collected for each sample at a resolution of 4cm\(^{-1}\) over the wavenumber region 4000-400 cm\(^{-1}\), using a Spectrum 100 (Perkin Elmer).

2.5.2 Differential scanning calorimetry (DSC)
Thermal analysis was carried out by DSC 4000 (Perkin Elmer). The sample of 8~9mg in weight was sealed in an aluminum pan and was heated from -60 to 60 °C at the heating rate of 10 °C/min under nitrogen gas flow of 20mL/min.

2.5.3 Thermo gravimetric analyzer (TGA)
Thermal data were obtained by using TGA 4000 (Perkin Elmer). The sample measurements were made between 25 and 600 °C at heating rate of 10 °C/min under nitrogen gas flow of 20mL/min.

2.5.4 Reometer
Curing characteristics were measured according to ASTM D2084 at 160°C on a MDR 2020 reometer, manufactured by Myung Ji Tech Co., Ltd. Scorch time (tsc2), optimum cure time (t90), minimum torque ,and maximum torque were determined.

2.5.5 Hardness Shore A
Hardness testing was tested according to ASTM D2240 on shore Durometer type A.

3 Results and discussion

3.1 FTIR spectroscopy
Figure 1 shows the infrared spectrum of 9-1 to 9-5 sample. The peak from 1745cm\(^{-1}\) to 1710cm\(^{-1}\) is attributed to the carboxyl group.

3.2 DSC curves
Figure 2 shows the DSC curves of ACM with different MEA content. The Tg of increases as increasing of MEA content.

3.3 TGA curves
Figure 3 shows the TGA curves of 9-1 to 9-5. The thermal onset temperature increases with the increasing of MEA content. It indicates the thermal stability is improved.

3.4 Oil Swelling Test
According to oil swelling test ASTM No1, each sample was aged 5 days. After this, each sample volume be calculated.

Table 2 shows the volume increase of ACM 9-1 to 9-5 and Table 3 shows the hardness shore A of ACM: (a) before crosslinking, (b) after crosslinking, and (c) after oil swelling. The hardness increases compared to without crosslinking. The oil swelling treatment reduces the hardness.

4 Conclusion
It can be concluded that polymerization of variate MEA show the close Tg. But the thermal property was improved. Oil swelling test result shows that the hardenss of ACM treated by oil swelling test is depended by the volume rate of increase. When the volume of increase is low, the change value of hardness is also very small.

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Figure 1. The infrared spectra of experiment.
Figure 2. DSC graph of ACM with different MEA content.

Figure 3. TGA curves of ACM with different MEA content.

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Table 1. Compounding Recipe of ACM

<table>
<thead>
<tr>
<th>Component/phr</th>
<th>Phr</th>
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<tbody>
<tr>
<td>Acrylic rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black</td>
<td>30</td>
</tr>
<tr>
<td>TETA</td>
<td>2</td>
</tr>
<tr>
<td>DCP</td>
<td>2</td>
</tr>
<tr>
<td>MBTS</td>
<td>1</td>
</tr>
<tr>
<td>DPG</td>
<td>1</td>
</tr>
<tr>
<td>BAPP</td>
<td>1</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
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Table 2. Volume Rate of Increase(%) of ACM with different MEA content

<table>
<thead>
<tr>
<th>Volume rate of increase(%)</th>
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<tbody>
<tr>
<td>9-1</td>
</tr>
<tr>
<td>9-2</td>
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<tr>
<td>9-3</td>
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<td>9-4</td>
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<tr>
<td>9-5</td>
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Table 3. hardness shore A of ACM: (a) before crosslinking, (b) after crosslinking, and (c) after oil swelling

<table>
<thead>
<tr>
<th>Shore A</th>
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<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>9-1</td>
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<tr>
<td>9-2</td>
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<tr>
<td>9-3</td>
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References