Performance of maleated castor oil based plasticizer on rubber: rheology and curing characteristic studies

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Abstract. The objective of this study was to evaluate the performance of maleated castor oil (MACO) as plasticizer on natural rubber (NR), ethylene propylene dien monomer (EPDM), and nitrile butadiene rubber (NBR). The parameter studied were involving rheological, curing and swelling properties. The MACOs were prepared by an esterification reaction between castor oil (CO) and maleic anhydride (MAH) with the help of xylene as water entrainer to improve water removal. Resulting oils then applied as a plasticizer in each of those rubbers within a fixed loading of 5 phr. Comparison has been made to evaluate the performance of MACO and conventional plasticizer (paraffinic oil for NR and EPDM, DOP for NBR) on each rubber. Rheology, curing characteristic and swelling of each rubber were studied. The results showed that rubber (NR/EPDM/NBR) plasticized with MACO had given similar flow characteristic to conventional plasticiizers. MACO exhibited slow curing, confirmed by higher $t_{90}$, but the scorch safety was of the same magnitude. MAH loading tended to decrease the flow properties and curing rate, while scorch time ($t_{5}$) was independent.

1. Introduction

The plasticizer, a low molecular weight substance, often added into rubber both to modify processing steps and final product properties. Petroleum-based plasticizers are widely used in rubber industries even though they give negative effect to the environment because of their toxic-polycyclic aromatic compound content. Some of those plasticizers also exhibit the tendency of leach out of material over time since they are not bonded covalently within polymer matrices [1]. The depletion of fossil feedstock and global warming issue are other problem that leads to exploring alternative materials. Vegetable-based oils are the potential candidates to substitute petroleum-based oil in this regard. This is mainly due to their nature of sources are renewable. Castor oil is potential candidates within this regard. It is a triacylglycerol containing one fatty acid, i.e. ricinoleic acid or 12-hydroxyoleic acid, that comprises over 89% of the fatty acid [2][3]. Castor oil is promising because it has unique molecular structure. Three functional groups are presented in its molecule, i.e. carboxylic groups, carbon double bonds (C=C) and hydroxyl groups [4]. These functional groups make the oil suitable for many chemical reactions and modifications.
Virgin castor oil needs to increase its compatibility with polymer matrices by modification [5]. Maleinization treatment through esterification with maleic anhydride is one of the modification route [2,6,7]. Maleated castor oil (MACO) is produced by esterification reaction of castor oil with maleic anhydride (MAH). Since esterification is an equilibrium reaction, thus high reaction yield can be achieved by shifting the chemical equilibrium toward the ester production. According to Le Chatelier principle, the yield and selectivity of the reaction product can be increased by the byproduct removal from the reaction system [8]. Previous studies have been successfully done but without water removal process[2,6,9]. Mazo et al., (2012) [10] compared conventional to microwave heating in MACO production. This study resulted in faster esterification reaction and showed the presence of the non-thermal effect of microwave heating. Unfortunately, this technology is rather difficult and expensive. Byproduct removal from reaction system was unclear. These are constituting a strong driving force to search for alternatives. Kulkarani and Sawant (2003) [11] carried out esterification of fatty acid using entrainer to enhance water removal. Direct esterification without solvent requires high temperature and resulted in the poor color product.

Recently, MACO is applied either as polymer matrices [6,12] or as polymer bio modifier [9,13], but application in therubber fields is limited. Dewi et al., (2016) [14] synthesized MACO and applied it on NBR/PVC blends. In the present study, MACO was synthesized from castor oil and maleic anhydride in various concentration, with the help of xylene as water entrainer. Xylene was used both to facilitate esterification reaction at low temperature and to enhance water removal. The resulting oils (MACO) were then applied as a plasticizer in natural (NR) and synthetic rubber (EPDM and NBR). Their effect on rubber rheology, curing characteristic and swelling properties in various solvents were evaluated.

2. Materials and Method

2.1. Material

Castor oil (Thai castor oil grade) and xylene were purchased from local market (PT. Brataco), while maleic anhydride (MAH) was obtained from PT. Justus Kimia Raya Indonesia. Natural Rubber (NR) grade Ribbed Smoke Sheet (RSS 1) supplied by PT. Perkebunan Nusantara IX (Indonesia). Nitrile Butadiene Rubber (NBR) as grade Kryvec 4975F and Ethylene Propylene Diene Monomer (EPDM) as grade Keltan 4551A. Each type of rubber was employed in 100 phr. Other materials used for compound preparation consist of carbon black grade N-330 (OCI, Korea) 30 phr and grade N-774 (OCI, Korea) 50 phr, zinc oxide(ZnO) 5 phr, aflux 42M (Rhein Chemie) 1 phr, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (Kemai) 1 phr, paraffin wax Antilux 65 A 0.5 phr, MBTS (Shandong Sianxian) 1.2 phr, TMTD 0.3 phr, and sulfur SP-325 (Miwon) 1.2 phr. All of rubber
compound materials were obtained from local market in industrial grade. Toluene and hexane (technical grade) were used as solvent.

2.2. Synthesis of Maleated Castor Oil

Our previous work [14] had been successfully synthesized MACO from castor oil and maleic anhydride with the aid of xylene as water entrainer. In this work, the mole ratio of CO and MAH was varied within a fixed ratio of CO/xylene 1:1 by weight. MC1-MC5 were denoted for MACO with various MAH loading as listed on Table 1. MACO was produced by an esterification reaction between CO and MAH. The reactions were carried out in a three-necked flask equipped with a dean stark apparatus and cold-water condenser. A mixture of castor oil and xylene were added into the three-necked flask and heated into 146°C. Then, add a portion of MAH incrementally into the mixture and the reaction was preceded for 5 h with continuous stirring 300 rpm. After the reaction completed, the solvent was removed by vacuum distillation. The effectiveness of esterification reaction was monitored by measuring acid value. Its determination was carried out by titration method using ethanolic KOH. The acid value was defined as expressed by equation 1. The functional groups before and after esterification were investigated using FTIR.

\[
\text{acid number} = \frac{56.1 VN}{w_{\text{sample}}} \quad \text{................. (1)}
\]

| Sample ID | Mole Ratio CO/MAH |
|-----------|------------------|
| MC1       | 1:1.0            |
| MC2       | 1:1.5            |
| MC3       | 1:2.0            |
| MC4       | 1:2.5            |
| MC5       | 1:3.0            |

2.3. Rubber Compound Preparation

Compounding recipes of mixes are following to previous section (material). Variations were made on the types processing oil of each rubber. For comparison, petroleum-based plasticizers were used, i.e. paraffinic oil for NR and EPDM, and DOP for NBR. All types of plasticizers were used in fixed amount of 5 phr. Compounding was carried out using laboratory two-roll mill. Finished compounds were then immersed in water in order to interrupt the premature crosslinking, which might be formed. Compounds were then allowed to mature for 24 h and stored in a dry place at a temperature of 25°C.

| Types of Plasticizer | Rubber |
|---------------------|--------|
|                     | NR     | EPDM  | NBR |
| Conventional        | R0     | E0    | N0  |
| MC1                 | R1     | E1    | N1  |
| MC2                 | R2     | E2    | N2  |
| MC3                 | R3     | E3    | N3  |
| MC4                 | R4     | E4    | N4  |
| MC5                 | R5     | E5    | N5  |
Notation of rubber compounds as seen in Table 2. Notation R0-R5 were denote for NR, while E0-E5 and N0-N5 were represented EPDM and NBR, respectively.

2.4. Curing Characteristic and Rheological Properties Measurement
Rheology and curing characteristics were studied using Moving Die Rheometer (MDR) Gotech 3000A at a frequency 100 cpm (cycle per minutes) and an angle 3 deg. For NR compounds, curing tests were performed at 150°C for NR and 170°C for EPDM and NBR. MDR experiment provided curing data such as scorch time ($t_s$) and optimum cure time ($t_{90}$). Rheology was studied by evaluating the viscous to the elastic ratio $(V/E)$. V/E ratio was represented by viscous $(S'')$ and elastic $(S')$ torques obtained from MDR [15].

2.5. Swelling Experiment
The swelling experiment was performed on 2x2 cm cut sample prepared by compression molding. The samples were immersed in two separated solvents, i.e. toluene and hexane, at 25°C for 24 h. The properties of solvent used in this experiment were listed on Table 3.

| Solvent | Molecular Weight | Molar Volume | Density ($\rho$), g/cm$^3$ | Solubility Parameter (δ), MPa$^{1/2}$ |
|---------|-----------------|--------------|---------------------------|--------------------------------------|
| Toluene | 92.14           | 106.29       | 0.867                     | 17.8                                 |
| Hexane  | 86.18           | 131.60       | 0.655                     | 13.2                                 |
| NR      |                 |              | 0.920                     | 16.6                                 |
| EPDM    |                 |              | 0.860                     | 15.0                                 |
| NBR     |                 |              | 0.970                     | 19.4                                 |

After the period was completed; the samples were taken out and blotted with filter paper to remove liquid on the surface. Swelling ratio ($Q_{t}$) is defined by Equation 2,

$$Q_{t}\% = \frac{w_{f} - w_{0}}{w_{0}} \times 100 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots

3. Result and Discussion
3.1. Properties of MACO
The effectiveness of esterification reaction was monitored by measuring acid value. Figure 1 depicts the changes in acid value during esterification reaction. The initial increase of acid number found in the early stage of reaction indicates the formation of free acid groups. Further progress reaction,
these groups are decreased because they took part in the formation of dimer, trimer or even oligomer [12]. Water formation might be indicated by cloud formation in the dean stark and is collected as separated phase [14]. With this regard, the resultant MACO was in the form of dimer or oligomer. Further analysis is needed to determine the molecular weight of the oil. An increasing mole of MAH causes the acid value to increase. The higher MAH loading, the higher amounts of the free acid group formed. Thus, higher acid value at one reaction time.

The MACO formation is also confirmed by the FTIR spectra as depicted in Figure 2. A broad peak is found at 3433 cm\(^{-1}\) which belong to hydroxyl (-OH) groups presents on the ricinoleic acid molecule. Another characteristic peak of CO is found at 1662 cm\(^{-1}\) which can be assigned to C-double bond stretching (–C=–C–) frequency. When CO reacts with MAH, the –OH peak is evidently decreased, while the double bond peak is enhanced. The peak at 1662 is found to be stronger along with increasing MAH mole in the reaction system, while –OH peak is more reduced even nearly disappear on CO:MAH=1:2 mole. These clearly reflect the more ester groups attached to the CO molecule chains. This finding is agreed with previous studies [2,6,13]. The cyclic anhydride peak at 1779 and 1849 cm\(^{-1}\)[12] is not observed in all spectra, indicating almost all of MAH were reacted with CO.

![Figure 1. Changes of acid value during esterification reaction](image1)

![Figure 2. Infrared spectra of pure CO, MC1, MC2 and MC3, MC4 and MC5](image2)

### 3.2. Curing Characteristic and Rheology

Figure 3a-c depicts the curing curve (plot torque versus time) of sample rubber compounds, while Table 4 summarizes the extracted data from curing curve on Figure 3. Curing curve is a powerful tool to study the crosslinking process and rheology of rubber compounds. This tool provides valuable information related to the processing characteristic that should be considered for subsequent processes. It is generally known that the curing curves can be divided into three stages (Figure 3a), i.e. induction
(I), curing (II) and over curing (III). The induction period is dominating by the viscous (plastic) behavior, thus give a brief description related to the processing safety. Both plasticizer, control, and MACOs, give similar induction period for each type of rubber. It can be said that MACO do not significantly affect to this period. EPDM samples exhibit longer induction period than two other rubbers.

![Curing curve (plot of rheometer torque vs time)](image)

**Figure 3.** Curing curve (plot of rheometer torque vs time) a) NR, b) EPDM, and c) NBR

During induction period, there is no chemical crosslinking formed. Interaction of rubber molecule chains with the filler particle surface or by chain entanglements produces physical crosslinking. This crosslink is reflected by the minimum elastic torque (ML) which is also related to the compound viscosity [16]. One can understand rubber flow behavior during processing by assessing this parameter [17]. It can be seen that MACO provides slightly higher viscosity than conventional plasticizer in NR compounds. This probably due to the interaction of functional groups on MACO with the rubber molecule chains. Bocqué et al., (2016) [5] explained that ester groups existed in vegetable-based oil interact via van der Waals bonding with the polymer chains and lead to a compatibilization with the polymer. But this effect is less pronounced in EPDM or NBR. MACO gives different response in NBR...
where the compounds viscosity is comparable. Compounds with higher viscosity should be treated carefully to avoid the defect during processing.

| Sample | MH (kgf·cm) | ML (kgf·cm) | MH-ML (kgf·cm) | S'MH (kgf·cm) | S'ML (kgf·cm) | tS2 (sec) | t90 (sec) | CRmax (kgf·cm/s) |
|--------|-------------|-------------|----------------|---------------|---------------|-----------|-----------|-----------------|
| R0*    | 54.83       | 2.66        | 52.17          | 1.74          | 3.28          | 40        | 87        | 82.46           |
| R1     | 55.34       | 3.33        | 52.01          | 3.59          | 3.89          | 39        | 117       | 60.47           |
| R2     | 57.61       | 3.76        | 53.85          | 3.15          | 4.45          | 52        | 140       | 54.88           |
| R3     | 57.13       | 3.96        | 53.17          | 3.24          | 4.56          | 48        | 135       | 56.89           |
| R4     | 42.48       | 2.41        | 40.07          | 3.93          | 3.25          | 47        | 136       | 39.76           |
| R5     | 52.78       | 3.13        | 49.65          | 3.42          | 3.82          | 50        | 137       | 51.15           |
| E0*    | 56.47       | 4.06        | 52.41          | 4.13          | 4.74          | 51        | 505       | 27.50           |
| E1     | 45.16       | 3.37        | 41.79          | 6.37          | 4.54          | 47        | 449       | 19.41           |
| E2     | 44.50       | 4.23        | 40.27          | 7.30          | 5.21          | 46        | 485       | 17.18           |
| E3     | 43.14       | 4.46        | 38.68          | 7.01          | 5.23          | 39        | 493       | 15.29           |
| E4     | 42.29       | 4.59        | 37.70          | 7.39          | 5.40          | 47        | 565       | 15.41           |
| E5     | 40.33       | 4.16        | 36.17          | 7.08          | 5.15          | 51        | 611       | 12.84           |
| N0*    | 68.09       | 5.24        | 62.85          | 15.28         | 6.24          | 21        | 319       | 90.75           |
| N1     | 59.76       | 5.17        | 54.59          | 15.91         | 5.94          | 20        | 331       | 62.91           |
| N2     | 62.84       | 5.72        | 57.12          | 16.73         | 6.52          | 22        | 358       | 70.64           |
| N3     | 58.21       | 5.61        | 52.60          | 15.84         | 6.37          | 25        | 283       | 65.84           |
| N4     | 60.63       | 5.55        | 55.08          | 15.69         | 6.35          | 27        | 202       | 72.59           |
| N5     | 68.58       | 5.64        | 62.94          | 16.43         | 6.34          | 23        | 125       | 75.21           |

*control: for NR and EPDM used paraffinic oil, while NBR used DOP

Chemical crosslinks are formed during curing period. The highest crosslink can be produced during vulcanization is described by the maximum elastic torque (MH). The differences between MH and ML thus qualitatively represents the apparent crosslink density of the rubber compound [18]. It is evidence that MHs are varied for each rubber used in this experiment. MACO provides lower MH than conventional plasticizer in EPDM, while gives comparable value in NR and NBR. Accordingly, the apparent crosslink densities are not influenced by the changes of MAH loading for NR and NBR, but it is greatly affected in EPDM. In over cure period, NR compounds exhibit typical reversion phenomenon. The introduction of MACO into NR mixes do not remove the reversion, but it slower the reversion occurrence (Figure 3a). Reversion is not occurred in EPDM and NBR.

Scorch time (tS2) is another important parameter to characterized the induction period because it gives a sign where vulcanization reaction begins. Scorch time has a strong correlation with the processing safety. The higher scorch time, the safer a process. Scorch time is also independent of the MAH concentration in MACO for non-polar rubber (NR and EPDM), but it tends to increase in polar rubber (NBR). The extent of curing often evaluates by assessing the optimum cure time (t90), in which most of the desired properties of the final product are achieved. Acidic nature of resultant MACO
affects the curing time retarded reaction. Slow reaction of MACO plasticized-NR is confirmed by lower cure rate maximum (CR\textsubscript{max}) achieved during vulcanization. EPDM show typical slow curing because of its low unsaturation on the backbone.

Flow properties of rubber compounds correlate to their viscosity. In rubber, viscosity rather complex since rubber is a viscoelastic material. Viscous (V) and elastic (E) elements are both existed at one time. During induction period, rubber compounds melt and flow once they are exposed to heat and pressure. Here, flow characteristic plays an important role and in turn determines the properties of the final product. Figure 4a-c shows the plot of $S''/S'$ versus time of the rubber samples. As expected, the domination of viscous element is observed in all rubber samples as observed from $S''>S'$. Rubber compound will have a better flow to fill the mold cavities before vulcanization started. When vulcanization begins, this domination is changed. Elastic element starts to rise as a result from chemical crosslinking. Compounds nearly stop to flow because the movements of rubber molecule chains are restricted by the crosslinks ($S''<S'$). The extent of each element domination finds to be different. The concentration of MAH in MACO influences either the $S''/S'$ ratio or the extent of domination of each element. It is probably affected by the higher compound viscosity and scorch time.

![Figure 4](image-url)
3.3. Swelling Characteristic

Swelling by immersion in the liquid is a powerful tool to evaluate the effect of liquid in rubber samples. When rubber contact with solvent, the molecules of solvent will penetrate into rubber matrix and causes rubber to swell. Two types of solvents were used in this study, i.e. toluene and hexane. The choice of these solvent was based on the nature of them. Toluene is aromatic, while hexane is aliphatic solvent. These two solvents have different ability in dissolving rubber [19]. Figure 5a-b shows the swelling results of all rubber samples in toluene and hexane after 24 h immersion. It is evident that all rubber samples exhibit positive mass changes after swelling for both solvents. It indicates no plasticizer leaching occurs.

![Figure 5a](image1.png)
![Figure 5b](image2.png)

**Figure 5.** Swelling percentage of rubber samples in a) toluene and b) hexane

All rubber samples show great affinity with toluene than that of hexane. This result may be attributed by higher molar volume of hexane compared to that of toluene (Table 3). Polar group of acrylonitrile (C≡N) group presents in NBR molecule chains interact strongly with the aromatic solvent [20] and results in high solvent sorption (high swelling percentage). On the other hand, NBR only provides weak interaction with the nonpolar hexane. Thus, low swelling percentage is observed.

4. Conclusion

MACO has been successfully synthesized and applied in NR, EPDM, and NBR. The resultant oils are predicted to be dimer or oligomer form, but acidic in nature. Application of MACO provides the different responses on rubber rheology, curing characteristic and swelling properties to each rubber, but those are comparable with the conventional plasticizer (paraffinic or DOP). On the rheology and curing properties, all rubber (NR/EPDM/NBR) plasticized with MACO had given similar flow characteristic to conventional plasticizers. MACO provides slightly higher viscosity than conventional
plasticizer in NR compounds, but less pronounced in EPDM or NBR. The apparent crosslink densities are not influenced by the changes of MAH loading for NR and NBR, but it is greatly affected in EPDM. Scorch safety seems to be independent upon plasticizer types and MAH loading in MACO and the acidic nature of resultant MACO affects the curing time retarded reaction. While on the swelling properties, MACO gives comparable swelling percentage to the conventional plasticizer. No plasticizer is found to leach out during swelling experiments.

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