Journal of Physical Science, Vol. 22(2), 1–14, 2011

Effect of Curing Systems on Thermal Degradation Behaviour of Natural Rubber (SMR CV 60)

Y. S. Rohana Yahya, A. R. Azura* and Z. Ahmad

School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal,
Seberang Perai Selatan, Pulau Pinang, Malaysia

*Corresponding author: azura@eng.usm.my

Abstract: *Different types of curing systems play important roles in the thermal degradation of natural rubber vulcanisates. In this study, natural rubber vulcanisates were cured with conventional (CV), efficient (EV) and Dicumyl Peroxide (DCP) curing systems at 160*^oC *using a laboratory-size two roll mill. The tensile, tear and swelling were tested before and after ageing for 2, 4, 6, 9 and 12 days at 100*^oC*. Fourier transform infrared (FTIR) measurements and thermogravimetric analyses (TGA) were performed to assess the thermal degradation behaviour of the natural rubber vulcanisates. The results indicated that the tensile modulus (M100), tensile strength, elongation at break and tear strength of the CV system were better compared to EV and peroxide systems before ageing. After ageing, the CV system vulcanisates, which contained predominantly polysulfidic linkages, showed drastically reduced tensile strength and elongation at break and tear due to crosslink breakage. Crosslink reformation into a stable network inhibited their ability to undergo strain-induced crystallisation at longer durations of ageing. The EV system vulcanisates showed comparable swelling index percentages before and after ageing while the peroxide curing system exhibited increased swelling uptake with longer ageing times. The presence of alcohol, amides and carbonyl groups after ageing was observed with FTIR measurements. Based on the TGA and DTG curves, the peroxide curing system vulcanisates showed higher thermal stability than the CV and EV curing system vulcanisates.*

Keywords: natural rubber (SMR CV 60), curing systems, heat ageing, thermal degradation

Abstrak: *Penggunaan sistem permatangan yang berbeza akan memberi kesan terhadap perubahan kelakuan degradasi terma getah asli. Dalam kajian ini, vulkanizat getah asli (SMR CV 60) telah disediakan menggunakan mesin penggiling bergulung dua dan dimatangkan dengan sistem pemvulkanan sulfur lazim (CV), sulfur cekap (EV) dan peroksida pada suhu 160*^oC*. Ujian tensil, cabikan dan pembengkakan telah dilakukan ke atas sampel–sampel getah asli sebelum dan selepas ujian penuaan haba selama 2, 4, 6, 9 dan 12 hari pada suhu 100*^oC*. Kajian ke atas perilaku degradasi terma dengan menggunakan spektroskopi transformasi Fourier inframerah (FTIR) dan analisa termogravimetri (TGA) telah dijalankan. Keputusan ujian menunjukkan sebatian getah asli yang dimatangkan dengan sistem CV mempunyai modulus tensil (M100), kekuatan tensil, pemanjangan takat putus dan kekuatan cabikan yang lebih tinggi berbanding sebatian sistem EV dan peroksida sebelum penuaan dilakukan. Selepas proses penuaan,* *sebatian sistem CV di mana ia mengandungi peratusan ikatan polisulfida yang tinggi telah mengalami penurunan secara mendadak bagi sifat–sifat kekuatan tensil, pemanjangan takat putus dan kekuatan cabikan disebabkan oleh pemutusan dan pembentukan semula sambung silang kepada rangkaian yang lebih stabil serta kehilangan kebolehan untuk menghablur di bawah terika pada masa penuaan yang panjang. Sebatian sistem EV menunjukkan peratus indeks pembengkakan yang hampir sama sebelum dan selepas ujian penuaan dilakukan, manakala, peratus indeks pembengkakan bagi sebatian yang dimatangkan dengan peroksida mengalami peningkatan dengan penambahan masa penuaan. Kehadiran kumpulan berfungsi iaitu alkohol, amida dan karbonil selepas ujian penuaan dijalankan dapat diperhatikan dengan menggunakan pengukuran FTIR. Berdasarkan kurva TGA dan DTG, sebatian sistem peroksida mempunyai kestabilan terma yang lebih tinggi berbanding sebatian CV dan EV.*

Kata kunci: Getah asli (SMR CV 60), sistem-sistem permatangan, ujian penuaan, degradasi terma

1. INTRODUCTION

Synthetic rubbers have been competing with natural rubbers for world market share since World War I. However, the continuous production of natural rubber has ensured its market position as a highly profitable crop despite the substantial resources from the synthetic rubber industry. Fluctuating oil prices, the main factor in the production of synthetic rubber, have contributed to natural rubber maintaining its market share. As the price of oil increases, natural rubber becomes a more attractive substitute.[1]

Natural rubber (NR) is chemically based on cis-1,4-polyisoprene, which is characterised by good elastic properties, resilience and damping behaviour but poor chemical resistance and processing ability. The unique mechanical properties of NR are due to the highly stereoregular microstructure resulting from its high molecular weight.[2] Its resistance to heat, oxygen and ozone is poor due to the presence of high number of double bonds in the chemical structure.[3] Further research on natural rubber degradation is therefore important.

Degradation of natural rubber can be caused by a variety of environmental factors, such as elevated temperature, humidity, impurities, mechanical load, irradiation and chemicals. In the presence of atmospheric oxygen, the useful lifetime of many polymer products is limited by oxidative reactions.[4] Radical attack of the polymer chain causes chain scission, crosslink formation and crosslink breakage. Changes in the properties of polymers with ageing depend on the extent of such reactions.[5]

Curing systems can influence the thermal degradation of natural rubber. Accelerated sulphur curing systems are commonly used in vulcanising the elastomers. The crosslink density and type of crosslink networks significantly influence the mechanical properties of the rubber vulcanisates. In general, the vulcanisates cured with efficient (EV) and conventional (CV) systems predominantly contain monosulphide, disulphide networks and polysulphide networks.[6] As an alternative, the peroxide curing system has been used to overcome this problem. The thermal stability of C-C linkages improves the ageing properties of elastomer compounds.[7]

Thermogravimetric analysis (TGA) is one of the most commonly used techniques to study the primary reactions of the decomposition of polymers and other materials. TGA is also useful for the characterisation and evaluation of polymer thermal stability. Although natural rubber has excellent mechanical properties, these properties may interfere with its low thermal stability. This may cause the polymer chain to be more susceptible to degradation. Degradation usually starts from a head-to-head structure, a site of unsaturation or a tertiary carbon atom.[8]

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) methods can be used for spectral characterisation of the physical properties of the prepared natural rubber compounds, as well as other complex samples such as polymer composites. The ATR-FTIR techniques allow analysis of specimens with minimum sample preparation and without solvent casting, grinding or pressing, as in the case in transmission experiments. Taking into account that the infrared radiation penetrates the sample to a few nanometers depth, the obtained information is characteristic for the surface of the sample.[9]

The objective of the present study was to analyse the effect of heat ageing on the mechanical properties of cured natural rubber. We used the CV, EV and DCP curing systems and took measurements before and after ageing for 2, 4, 6, 9 and 12 days at 100°C. Swelling, ATR-FTIR and TGA were also used to assess the thermal degradation of the natural rubber compounds.

2. EXPERIMENTAL

2.1 Materials

Natural rubber (SMR CV 60) was purchased from the Rubber Research Institute of Malaysia (RRIM). Zinc oxide, stearic acid, N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) and sulphur were obtained from Bayer Sdn. Bhd.

2.2 Sample Preparation

Formulations for the rubber compounds are given in Table 1. The rubber compounds were mixed using a laboratory-sized two-roll mill (Model XK-160) according to ASTM D3184. The samples were compression molded at 160°C with a cure time of t_{90} obtained from an oscillating disc rheometer (MDR 2000) according to ASTM D2084.

Table 1: Formulation of natural rubber cured with CV, EV and DCP curing systems.

Ingredients	CV	EV	EV
Natural rubber	100	100	100
Zinc Oxide	5	5	-
Stearic acid	2	2	-
CBS	0.6	5	-
Sulfur	2	0.5	-
DCP	-	-	2

2.3 Tensile and Tear Properties

For the tensile tests, dumbbell specimens 2 mm thick were cut from compression-molded sheets. The tensile properties of the specimens were measured according to ASTM D 412 using a tensometer (Model T10). A crosshead speed of 500 mm/min was used for the tensile tests. To test for the tear strength, we referred to ASTM D624 and used a crosshead speed of 100 mm/min.

2.4 Ageing Properties

To measure the heat ageing resistance, we conducted tests for 2, 4, 6, 9 and 12 days at 100°C according to ASTM 572. The aged specimens were left at room temperature for at least 16 hours before the mechanical properties are tested.

2.5 Swelling Index Measurement

For the swelling index measurements, small pieces of the vulcanisates with a total weight of approximately 0.3 g were immersed in 25 ml of toluene for 24 hours at room temperature. The swollen specimens were blotted with filter paper and weighed. The swelling index percentages were determined by using Equation 1, where Wu and Ws are the weights of the unswollen and swollen rubber, respectively.

$$\text{Swelling index (\%)} = \frac{Ws - Wu}{Wu} \times 100 \qquad (1)$$

2.6 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR)

The ATR-FTIR experiments were performed at room temperature for natural rubber samples before and after ageing. The spectral curves were acquired at wavenumbers of 4000–550 (cm^{-1}) in reflectance mode.

2.7 Thermogravimetric Analysis (TGA)

The TGA of 10 mg of natural rubber samples was carried out using a Perkin Elmer Analyzer with a temperature range of 30–600°C at a heating rate of 10^{o}C/min.

3. RESULTS AND DISCUSSION

3.1 Curing Characteristics

Table 2 shows the curing characteristics of natural rubber using different types of curing systems. The scorch time (t_{s2}) is the time required for the minimum torque value to increase by two units and measures the premature vulcanisation of the material. The optimum cure time (t_{90}) is the vulcanisation time for optimum physical properties and corresponds to the optimum cure torque. The EV system exhibited shorter t_{s2} and t_{90} values than the CV and DCP curing systems due to the high accelerator concentration; therefore, more crosslinks are formed in shorter time.[10] The minimum torque in a rheograph measures the viscosity of the vulcanisates, and the maximum torque is generally correlated with the stiffness and crosslink density. The DCP curing system vulcanisates exhibited higher values of minimum torque M_L and maximum torque M_H compared to the accelerated sulfur curing systems. The rigid C-C structure in the peroxide system offers more resistance to the rheometric torque.[11]

Table 2: Curing characteristic of natural rubber cured with CV, EV and DCP curing systems.

Type of curing systems	T_{s2} (min)	T_{90} (min)	M_L (dNm)	M_H (dNm)
CV	3.89	8.82	0.16	5.70
EV	3.16	5.62	0.15	6.09
DCP	3.52	14.98	1.00	6.22

3.2 Mechanical Properties

Tensile properties are commonly used to measure the degradation behaviour of elastomers. As shown in Figure 1, all compounds showed similar tensile modulus (M100) values before ageing. The M100 values of the vulcanisates cured with the CV system were decreased after 4 days of ageing and started to increase after 6 days of ageing. By contrast, the EV system vulcanisates exhibited increased M100 values with increasing ageing times. The DCP system vulcanisates showed the opposite behaviour with decreasing tensile modulus values with longer ageing times. The modulus is related to the crosslinking density of the rubber vulcanisates. These changes are directly associated with changes in the original crosslink structure, such as main chain scission and crosslink modifications.[4,12]

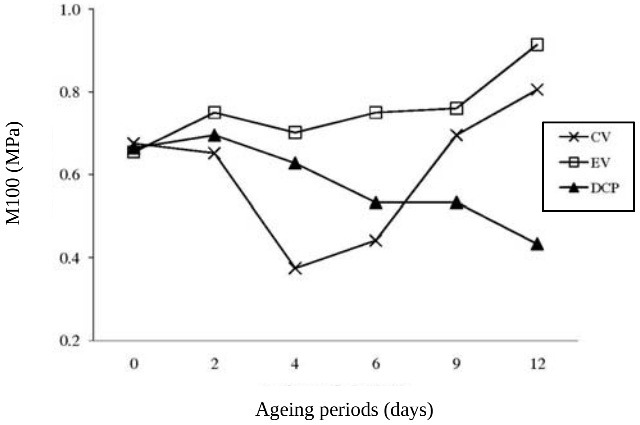


Figure 1: Tensile modulus values of natural rubber cured with CV, EV and DCP curing systems before and after ageing for 2, 4, 6, 9 and 12 days at 100°C.

The tensile strength, elongation at break (EB) and tear strength values for natural rubber cured with different types of curing systems are illustrated in Figures 2–4. The tensile strength, EB and tear strength values of the CV system vulcanisates were higher than the EV and DCP system vulcanisates before ageing. The weak crosslinks, especially polysulphide crosslinks, can slide past each other, allowing relaxation at high stress concentrations. The stresses are distributed uniformly, resulting in high tensile and tear properties compared to monosulphide, disulphide and C-C linkages.

The tensile strength, tear strength and EB values decreased with longer ageing times, especially for natural rubber vulcanisates cured with the CV system. During the earlier stages of heat ageing, crosslink scissions and the formation of new crosslinks into the stable networks affected these properties. The CV system vulcanisates had a high content of polysulphide linkages with a low bond strength. By contrast, monosulphide linkages have relatively strong bond strength and are dominant in the EV system vulcanisates.[13] As a result, the CV system exhibited a weaker thermal ageing resistance than the EV system. Monosulphide, disulphide and C-C linkages have higher thermal stability than polysulphide crosslinks.

The EV system vulcanisates showed better ageing resistance than the DCP system vulcanisates. The DCP system vulcanisates supposedly exhibit good ageing properties; however, we observed that the samples became tacky and the voids appeared after exposure to high temperatures with increasing ageing time. According to Baker,[14] natural rubber softens and weakens at high temperatures, loses its strength and becomes tacky. These changes might occur due to reduced crosslink formation between the polymer chains of natural rubber. After ageing for 4 days and longer, natural rubber cured with the CV and DCP systems exhibited inferior tensile strength values and became constant, which explained the loss of ability to crystallise. During extended periods of heating, the excessive main chain scission and/or modifications resulted in a reduced tendency to crystallise at high elongation.[15]

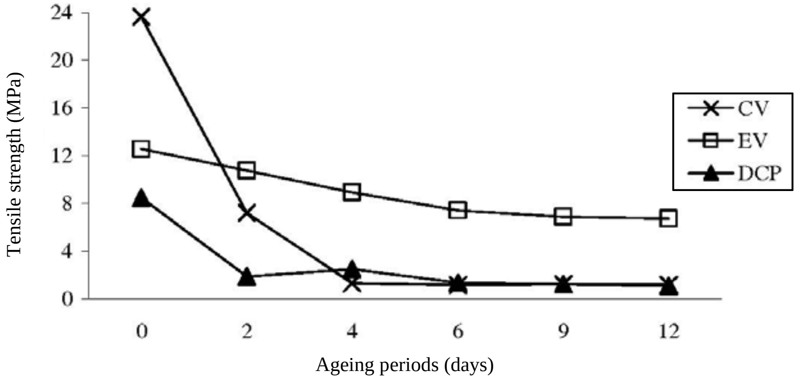


Figure 2: Tensile strength values of natural rubber cured with CV, EV and DCP curing systems before and after ageing for 2, 4, 6, 9 and 12 days at 100°C.

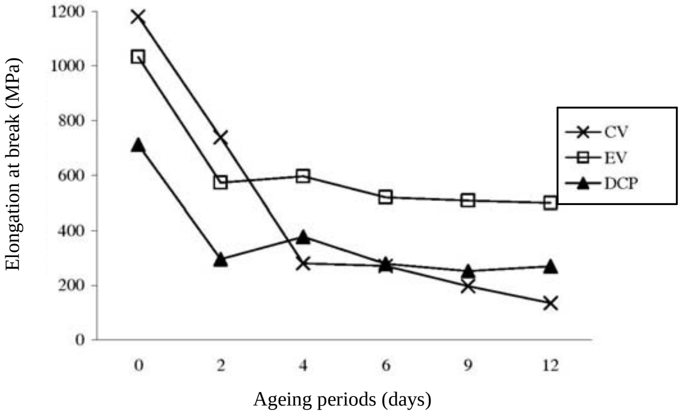


Figure 3: Elongation at break percentages of natural rubber cured with CV, EV and DCP curing systems before and after ageing for 2, 4, 6, 9 and 12 days at 100°C.

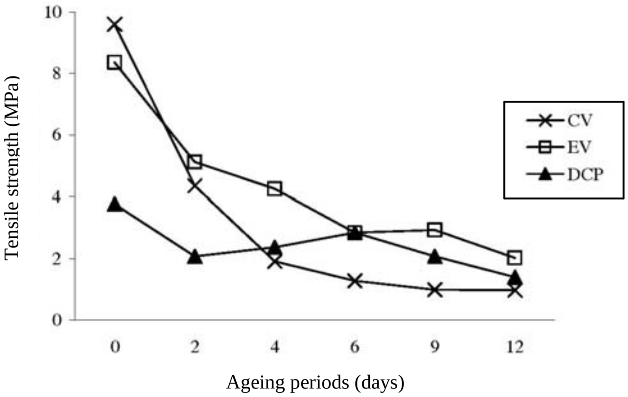


Figure 4: Tear strength values of natural rubber cured with CV, EV and DCP curing systems before and after ageing for 2, 4, 6, 9 and 12 days at 100°C.

3.3 Swelling Index Measurements

The results shown in Figure 5 indicated that the CV system vulcanisates exhibited irregular trends, while the swelling behaviour of the EV system vulcanisates did not change significantly with longer ageing time. The swelling index percentages are related to the crosslink density of the elastomers. When the rubber was exposed to high temperature for longer period, oxygen molecules in the air will diffuse into the surface, but some of them were immediately consumed by oxidation reactions to produce crosslinking, scission of the rubber chains or crosslinks and combination with molecular chains of rubber. Therefore, the crosslink density changed with curing, especially in the CV system vulcanisates.[16,17] For the DCP curing system vulcanisates, the swelling index percentages increased after ageing. In theory, it is difficult for solvent molecules to penetrate the carbon linkages (C-C) because of strong bonding and high rigidity.[17] However, in this study, solvent molecules easily penetrated into the DCP vulcanised samples because the number of C-C bonds per unit volume decreased with longer ageing times.

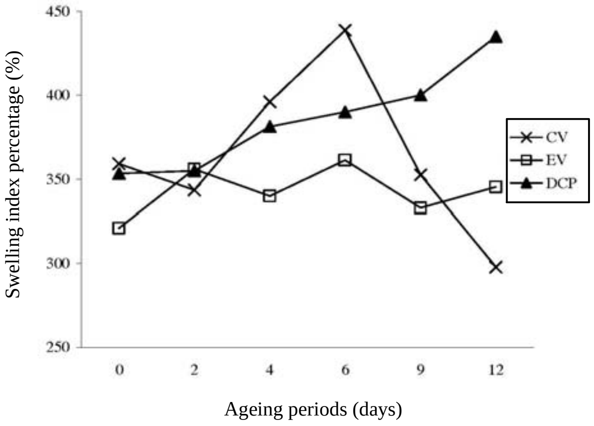
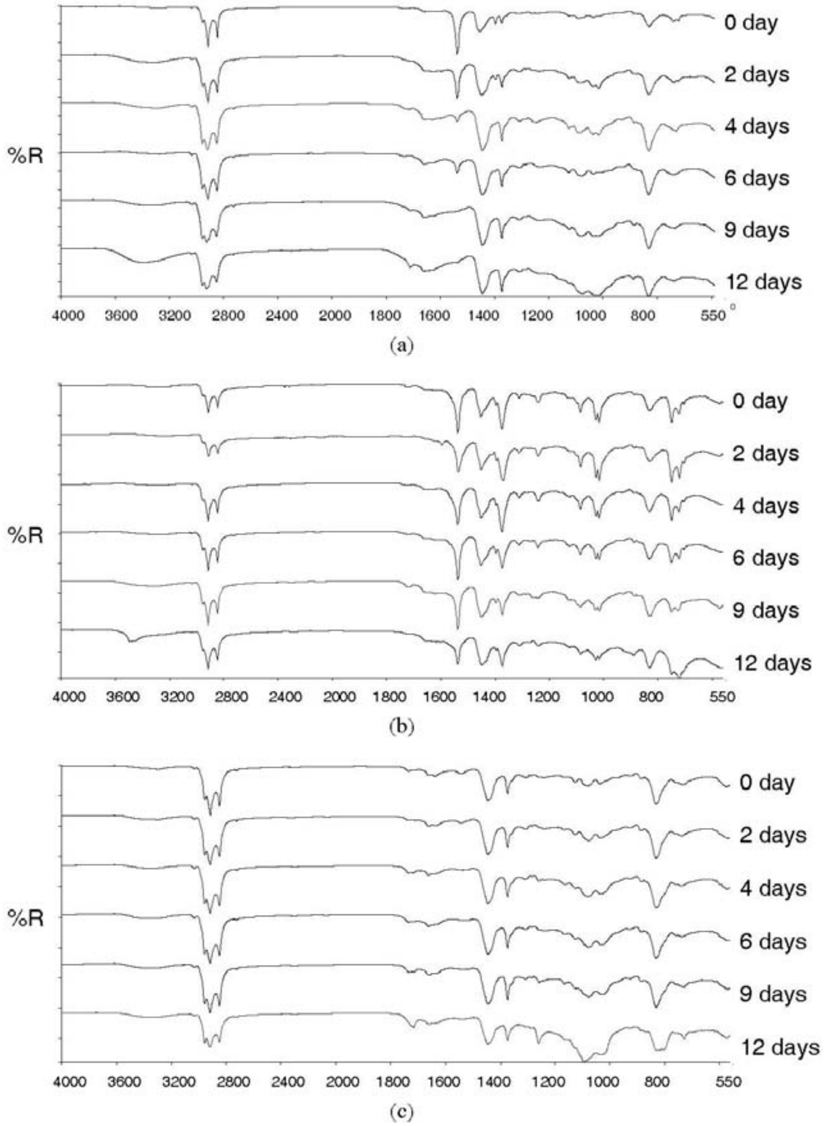


Figure 5: Swelling index percentages of natural rubber cured with CV, EV and DCP curing systems before and after ageing for 2, 4, 6, 9 and 12 days at 100°C.

3.4 Fourier Transform Infrared (FTIR)

As shown in Figures 6(a), (b) and (c), the FTIR spectra of all natural rubber vulcanisates cured with different curing systems showed strong bands in the range of 3015–2744 cm^{-1} before and after ageing, indicative of the asymmetric and symmetric stretching frequency of the C-H groups (C-CH$_3$ and –CH$_2$–). In addition, strong bands were observed for all vulcanisates at 1488–1398 cm^{-1} and were attributed to chain scission of the C-H groups. Natural rubber cis-isomer configurations can be observed at 870–780 cm^{-1}. The –OH groups appeared at 3567–3157 cm^{-1}, especially after 12 days of ageing.[18] The bands at 1485–1340 cm^{-1} bands were attributed to amide groups (–NH2) produced by the accelerated sulphur curing systems due to the use of CBS as the accelerator. The CV system vulcanisates exhibited decreased reflectance percentages with longer ageing periods. The presence of C=O groups observed in the 1808–1683 cm^{-1} region for all vulcanisates was due to oxidation at the main polymeric chain, especially after 12 days of ageing.[19] The strong bands in the range of

1171–935 cm^{-1} for natural rubber cured with the EV system indicated the formation of a high content of C-S stretches in this system.



(a)

(b)

(c)

Figure 6: FTIR analysis measurements of natural rubber cured with CV, EV and DCP curing systems before and after ageing for 2, 4, 6, 9 and 12 days at 100°C, which are (a) CV, (b) EV and (c) DCP curing systems.

3.5 Thermogravimetric Analysis (TGA)

The TGA mass loss curves of samples of natural rubber cured with CV, EV and DCP curing systems are shown in Figure 7. The onset temperatures of decomposition can be calculated from TGA curves by extrapolating the curve at the initial mass loss of the natural rubber compounds. From the derivatives of the thermogravimetry curves [the DTG curves, Figure 7(b)], the maximum decomposition data can be used to determine the temperatures of degradation. Table 3 shows the temperatures of the initial decomposition or onset and the maximum decomposition of the natural rubber vulcanisates. The initial decomposition temperature is used to predict the thermal stability of the rubber vulcanisates. The initial decomposition temperature of the DCP-cured vulcanisates was higher than that of the accelerated sulphur curing system vulcanisates due to the stability of the C-C linkages.[8] The maximum decomposition temperatures of all the compounds were similar as they contain the same type of elastomer.

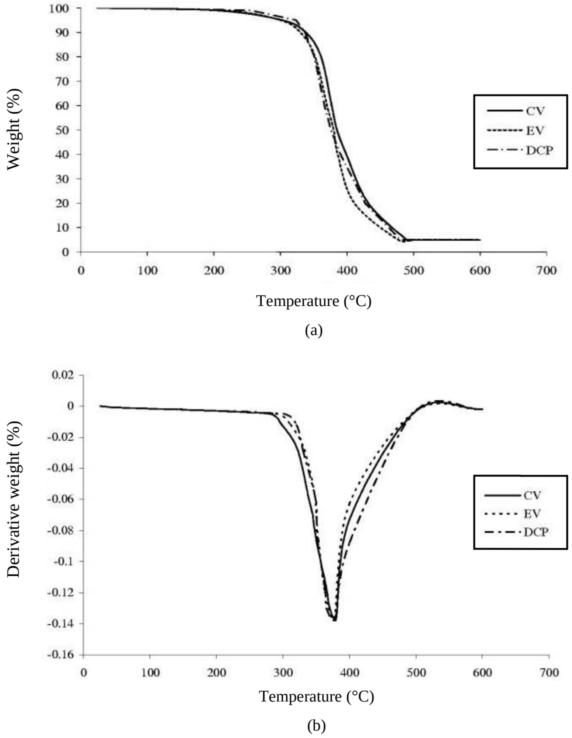


Figure 7: (a) TGA and (b) DTG curves of natural rubber cured with CV, EV and DCP curing systems.

Table 3: Initial decomposition temperature and maximum decomposition temperatures of natural rubber cured with CV, EV and DCP curing systems.

Samples	Initial decomposition temperature (°C)	Maximum decomposition temperature (°C)
CV	203	380
EV	217	377
DCP	255	379

4. CONCLUSION

Before ageing, the different types of crosslinks determine the properties of natural rubber. After ageing, changes in the crosslink densities negatively affect the tensile and tear properties. Crosslink breakage and reformation in natural rubber cured with CV systems led to scission and modification of the chains, thus reducing their strain-induced crystallisation. The EV system vulcanisates showed comparable properties before and after ageing due to the stability of the mono- and di-sulphide lingkages. The crosslink density of the DCP curing system vulcanisates decreased with longer ageing durations and affected the performance of the samples. Using FTIR spectroscopy, we observed alcohol and carbonyl groups for all vulcanisates, especially after 12 days of ageing. An amide group was produced in accelerated sulphur curing system vulcanisates due to the presence of CBS as an accelerator. The formation of alcohol and carbonyl groups in the rubber vulcanisates decreased the mechanical properties of the natural rubber vulcanisates. Based on the TGA study, we conclude that the DCP curing system led to higher thermal stability than the accelerated sulphur curing system vulcanisates.

5. ACKNOWLEDGEMENTS

The authors acknowledge the Ministry of Higher Education (MOHE) for a research grant (FRGS-6071106) and Universiti Sains Malaysia for providing research facilities.

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