

Research article

Influence of vulcanization system on curing, mechanical, dynamic and morphological properties of maleated natural rubber and its thermoplastic vulcanizate with thermoplastic copolyester elastomer

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Abstract. Maleated natural rubber (MNR) was prepared and compounded with four alternative vulcanization systems: sulfur, peroxide, phenolic, and mixed sulfur-peroxide vulcanization systems. It was found that the peroxide and mixed sulfur-peroxide cured systems show a plateau curing curve, while the sulfur-cured system exhibits reversion, and the phenolic cured system gives marching cure behavior. Also, thermoplastic vulcanizates (TPVs) based on dynamically cured MNR and thermoplastic copolyester elastomer (TPC-ET) blends (*i.e.*, MNR/TPC-ET TPVs) by using these vulcanization systems were also prepared and characterized. The height and area underneath the dynamic vulcanization peaks in the mixing torque-time curves directly relate to the degree of vulcanization and strength along with the nature of crosslink structures, and these had the rank order peroxide > mixed sulfur-peroxide > phenolic > sulfur by vulcanization system. This is in good agreement with the maximum torque, tensile strength, hardness, moduli, and toughness of MNR compounds. The locations of the peaks also correspond to the scorch time (t_{s1}), and the sulfur and phenolic cured systems with scorch times of 2.31 and 2.44 min showed peaks at 3.3 and 3.4 min, respectively, offering improved process safety. The sulfur-cured TPV had sulfidic linkages and the smallest-sized vulcanized rubber domains, giving it the highest tensile strength, elongation at break, storage modulus, and rubber elasticity (*i.e.*, the lowest tension set and $\tan\delta$). However, the phenolic cured TPV had the highest stiffness, Young's modulus, and large vulcanized rubber domains, which relate to low content of Chroman ring structures in the crosslinked MNR vulcanizates, with a comparatively low interfacial area and hence weak interfacial interactions between MNR and TPC-ET phases. Furthermore, the mixed sulfur-peroxide and peroxide curing systems gave intermediate tension set, $\tan\delta$, and elongation at break.

Keywords: maleated natural rubber (MNR), thermoplastic copolyester elastomer (TPC-ET, COPE), vulcanization system, dynamic properties, morphological properties

1. Introduction

Natural rubber (NR) from *Hevea brasiliensis* trees has been well-known as a renewable bio-based polymer that has been widely used in a wide variety of applications. NR molecules inside the latex rubber particles consist of the proteins with trans-1,4-isoprene units (*i.e.*, α -terminals) connected to a long sequence

of cis-1,4-polyisoprene along with phospholipid at the ω -terminals [1–3]. Therefore, NR is an attractive renewable bio-based elastomer that is non-toxic. It has excellent physical properties, including high elasticity, mechanical strength, fatigue resistance, and tear strength, together with environmental friendliness. NR is the most used elastomer worldwide industrially,

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in a variety of applications, due to its low price and good elastic, mechanical, and damping properties. However, NR has some limitations, including poor resistance to hydrocarbons, fats, oils, and greases and poor ozone and weathering resistance together with incompatibility with polar polymers [4]. Chemical modifications of NR molecules could be used to improve the NR properties and extend the scope of NR applications. Succinic anhydride grafted natural rubber, or maleated natural rubber (MNR), is considered to be one of the important NR derivatives that can be used to enhance blend [5, 6] and composite [7, 8] properties.

Thermoplastic elastomers (TPEs) are materials that combine the properties of thermoplastics and soft elastomers, but they can be processed and recycled as thermoplastics [9]. TPEs offer a variety of advantages over conventional thermoset (vulcanized) rubber materials, such as simpler processing with fewer steps and shorter fabrication times, which lead to lower finished part costs, little or no compounding process, reuse of scrap in the same fashion as with thermoplastics, and lower energy consumption and cost due to shorter molding cycles and simpler processing [10]. Commercially available TPEs, based on chemical composition and morphology, can be categorized into eight different groups: styrenic block copolymers (SBCs), polymer blends by dynamic vulcanization (TPVs), polyolefin-based thermoplastic elastomers (TPOs), halogen-containing polyolefins, thermoplastic polyurethane elastomers (TPUs), polyamide-based thermoplastic elastomers (COPA), polyether ester elastomers (COPE), and ionomeric thermoplastic elastomers [11]. Therefore, there are two common types of TPE materials based on blending rubber with thermoplastics: simple blends (SBs), such as polyolefin-based thermoplastic elastomers (TPOs), and thermoplastic vulcanizates (TPVs) [12]. Simple blends are typically prepared by blending the polymer pair without the addition of any curative, and the blend ends up having a co-continuous phase structure. In contrast, to prepare a TPV via dynamic vulcanization, curing agents or a vulcanization system are applied to the rubber phase while it is blended with the thermoplastic at an elevated temperature [13]. Generally, the mechanical, morphological and other useful related properties of TPVs mainly depend on various parameters, including blend composition [13–16], compatibility between the blend

components [17–20], phase morphology [21–24], and vulcanization system [14, 21, 22]. Various vulcanization systems have been exploited to vulcanize the rubber phase during dynamic vulcanization of rubber/thermoplastic blends to form TPV materials, for instance, sulfur [12, 15, 20, 21, 24], peroxide [14, 18, 21, 23, 25], phenolic [16, 19, 21, 22], bismaleimide [21, 25, 26], sulfur donor [17, 27], and coagents sulfur and bismaleimide [21]. Different vulcanization systems typically provide different cross-link structures, morphological properties, sizes of vulcanized rubber domains, and mechanical, dynamic, and other structure related properties.

Natural rubber (NR) is typically used as one possible elastomeric component in a TPE, which is then generally called thermoplastic natural rubber (TPNR) [28]. Besides the normal NR form, chemically modified NRs such as epoxidized natural rubber (ENR) and maleated natural rubber (MNR) have also been used to prepare TPNR, owing to their unique properties, high polarity, good compatibility with polar thermoplastics, and air impermeability. There are many kinds of thermoplastics that have been used to prepare TPNR based on blending with MNR, such as polypropylene [29–31], poly(lactic acid) [32, 33], sulfonated polystyrene [34, 35], high-density polyethylene [36], and poly(methyl methacrylate) [37].

The main aim of this research study was to assess the influences of alternative vulcanization systems on the curing, mechanical, rheological, and dynamic properties of MNR vulcanizates based on static vulcanization. The four different vulcanization systems used were sulfur, peroxide, phenolic, and mixed sulfur-peroxide vulcanization systems. Then, the dynamically cured TPC-ET/MNR blends were prepared with the alternative vulcanization systems, with the main aim being to prepare TPV materials with high damping and other related properties at a low hardness (*i.e.*, lower than 80 Shore A). This is because TPC-ET, with low hardness, is not appropriate for industrial applications due to its very poor damping properties. The addition of a high damping material component with some polarities and decent elastic properties, like MNR, could improve the elasticity and damping properties of TPC-ET materials. These new materials might be suitable for various industrial applications, such as appliances and automotive parts (interior and exterior), demanding both elasticity and strength.

2. Experimental

2.1. Materials

Natural rubber, Standard Thai Rubber (STR 5L) with Mooney viscosity (ML1+4, 100 °C) range 70–75, was manufactured by Tavorn Rubber Industry (1982) Company Limited (Songkla, Thailand). It was used as a raw material to prepare maleated natural rubber (MNR) by the preparation and characterization procedures described in our previous work [38, 39]. Maleic anhydride (MA) used in the preparation of maleated natural rubber (MNR) was manufactured by Fluka Chemika Co., Ltd (Buchs, Switzerland). Thermoplastic copolyester elastomer (TPC-ET), Hytrel® G3548L, was manufactured by DuPont (Wilmington, USA). It is a block copolymer consisting of a hard (crystalline) segment of polybutylene terephthalate and a soft (amorphous) segment based on polyether chemistry. Hytrel® G3548L is a low modulus grade with a nominal durometer hardness of 35D, melt flow index (MFI) of 10 g/10 min (190 °C, 2.16 kg, ISO 1133) and shear viscosity at a shear rate of $1000 \text{ s}^{-1} = 135 \text{ Pa}\cdot\text{s}$ (190 °C). The zinc oxide used as an activator in the sulfur curing system was manufactured by Global Chemical Co., Ltd (Samut Prakarn, Thailand). The stearic acid used as an activator was manufactured by Imperial Chemical Co., Ltd (Pathum Thani, Thailand). Wingstay® L was used as a highly effective polyphenol antioxidant, supplied by Synthomer plc (London, UK). The sulfur used as a vulcanizing agent was manufactured by Siam Chemicals Co., Ltd, (Samut Prakarn, Thailand). The *N*-tert-butyl-2-benzothiazolesulphenamide (Santocure TBBS) used as an accelerator was manufactured by Flexsys Chemicals Belgium NV (Antwerp, Belgium). The Santoflex 6PPD (*N*-phenyl-*N'*-1,3-dimethylbutyl-*p*-phenylenediamine) used as an antioxidant was manufactured by Flexsys Chemicals

Belgium NV (Antwerp, Belgium). Dicumyl peroxide (DCP) used as a curing agent of MNR was manufactured by Wuzhou International Co., Ltd., (Wuxi, China). Triallyl cyanurate (TAC) was used as a co-agent in the peroxide curing system and was manufactured by Fluka Chemie GmbH (Buchs, Switzerland). The dimethylol phenolic resin with active hydroxymethyl (methylol) groups, grade HRJ-10518 (made by reacting octylphenol and formaldehyde), was used as a phenolic curing agent and was manufactured by Schenectady International Inc., (New Port, USA).

2.2. Preparation of maleated natural rubber compounds with various vulcanization systems

Maleated natural rubber (MNR) was first prepared in-house, as described in our previous work [38, 39]. It was then compounded with the various vulcanization systems (*i.e.*, sulfur, peroxide, phenolic, and mixed sulfur-peroxide systems) by using chemical ingredients, as shown in Table 1. The compounding of rubber and chemicals was performed in an internal mixer, Brabender® Measuring Mixers, model 50EHT 3Z, Brabender® GmbH & Co. KG, (Duisburg, Germany) at 40 °C, and at rotor speed 60 rpm according to the mixing schedule in Table 2. After dumping the rubber compound from the mixing chamber, it was further homogenized by passing through the 1 mm nip of a CT two-roll mill, Charoen TuT Co., Ltd. (Samut Prakarn, Thailand) with a friction ratio of 1:1.25 at ambient temperature for about 5 min. Then, cure characteristics of the MNR compound were analyzed by using a moving die rheometer (MDR), Rheo Tech MDPT, Tech Pro Inc, (Cuyuhoga Falls, USA) at 170 °C. The MNR compound was eventually fabricated to a thin sheet of about 2 mm thickness

Table 1. Compounding formulation of maleated natural rubber (MNR) with various vulcanization systems.

Chemical	Quantity [phr]			
	Sulfur	Peroxide	Phenolic	Mixed sulfur-peroxide
MNR	100	100	100	100
ZnO	5	5	5	5
Stearic acid	1	1	1	1
6PPD	1	1	1	1
TBBS	1	–	–	0.5
Sulfur	3.5	–	–	1.75
DCP	–	2	–	1
TAC	–	1	–	0.5
HRJ-10518	–	–	7	–

Table 2. Mixing schedule for compounding of maleated natural rubber (MNR) with various vulcanization systems.

Description	Mixing time [min]			
	Sulfur	Peroxide	Phenolic	Mixed sulfur-peroxide
Mastication	2	2	2	2
Stearic acid	1	1	1	0.5
ZnO	1	1	1	0.5
Wingstay® L	1	1	1	0.5
TBBS	1	–	–	1
Sulfur	1	–	–	1
DCP	–	1	–	1
TAC	–	1	–	1
HRJ-10518	–	–	1	–

by compression molding, using a compression molding machine model IA, Chaicharoen Karn Chang, Ltd., (Bangkok, Thailand) at 170 °C and high pressure for the respective cure time based on the MDR test.

2.3. Influence of vulcanization system on properties of dynamically cured MNR and thermoplastic copolyester elastomer blends

Dynamically cured MNR/TPC-ET blends or MNR/TPC-ET TPVs were prepared by blending MNR compounds with a different vulcanization system (sulfur, peroxide, phenolic, or mixed sulfur-peroxide system) (Table 1) and thermoplastic copolyester elastomer (TPC-ET) via dynamic vulcanization at the fixed 50/50 w/w blend proportions of MNR and TPC-ET. This blending ratio was selected due to the closed shear viscosities of MNR and TPC-ET with the viscosity ratio ($\eta_{\text{MNR}}/\eta_{\text{TPC-ET}}$) of 1.12 (shear viscosity at a shear rate of 1000 s⁻¹ of MNR = 152 Pa·s at 190 °C)). Blending was performed in an internal mixer, Brabender® Measuring Mixers, model 50EHT 3Z, Brabender GmbH & Co. KG, (Duisburg, Germany) at 170 °C, with a rotor speed set at 60 rpm and using a fill factor of 0.85. The TPC-ET was first dried in a hot air oven at 80 °C for at least 2 h to eliminate moisture. It was then incorporated into the mixing chamber and mixed for about 2 min at 170 °C. The MNR compound was then added into the mixing chamber with continued blending until a plateau mixing torque or the total mixing time of 12 min was reached. The blended product was then dumped from the mixing chamber, conditioned at room temperature for at least 3 h, and then ground to small particles by using a plastic grinder machine, Bosco Engineering

Co., Ltd., (Bangkok, Thailand). The MNR/TPC-ET TPV was then fabricated by plastic injection molding machine with a clamping force of 90 tons, model TII-90F, Weltec Machinery Ltd., (Hongkong, China) fitted with standard tensile specimens mold in accordance with ISO 37. The temperature was set for different zones of injection molding at 160, 165, 170 and 170 °C in heating barrel zones 1, 2, 3 and injection nozzle, respectively. Also, the injection pressure was set in the common range between 90 to 110 MPa. Mechanical, morphological, and dynamic properties of the dynamically cured MNR/TPC-ET were eventually characterized.

2.4. Characterization

2.4.1. Cure characteristics

Cure characteristics of the MNR compound were determined at 160 °C by using a moving die rheometer (MDR), rheoTech MD⁺, Tech Pro Inc., (Cuyahoga Falls, USA) at a fixed frequency of 1.67 Hz, and a strain amplitude of 1° arc at 170 °C. The optimum scorch time (t_{s1}), cure time (t_{c90}), minimum torque (M_L), maximum torque (M_H), and torque difference ($M_H - M_L$) were determined from the curing curves.

2.4.2. Mechanical properties

The 50/50 MNR/TPC-ET TPVs pellets were fabricated to dumbbell-shaped specimens by injection molding using a Weltec thermoplastic injection-molding machine, Weltec Machinery, Ltd., (Hongkong, China) with a clamping capacity of 90 tons. Tensile properties in terms of tensile strength, elongation at break, and tension set of MNR vulcanizates and MNR/TPC-ET TPVs were tested with a Hounsfield tensometer, model H 10 KS, Hounsfield Test Equipment Co., Ltd., (Raydon, UK) at a crosshead speed of 500 mm/min and at a room temperature according to ISO 37. Aging properties of the MNR/TPC-ET TPVs were also determined after accelerated aging at 100 °C for 22 h in a multi-cell aging oven, model Elastocon AB, Elastocon Inc, (Rämhult, Sweden), according to ASTM D 573. After removal from the oven, the samples were conditioned at room temperature for at least 24 h before the tensile strength and elongation at break were determined and compared to the ones before aging. The tension set was determined according to ASTM D412 by extending the dumbbell shape specimen to 100% elongation and left at this position for 10 min before releasing. The specimen was then allowed to recover for another 10 min before

measuring the length compared to the original length, where the % tension set was evaluated. The hardness of the MNR vulcanizates was determined by a durometer Shore A, model S1 Digital Durometers, An Instron Company, (Massachusetts, USA) according to ISO 48.

2.4.3. Morphological properties

Morphological studies of MNR/TPC-ET TPVs were carried out by using a scanning electron microscope (SEM), model Quanta 400, FEI company (Hillsboro, USA). Injection-molded samples of the MNR/TPC-ET TPVs were first cryogenically fractured in liquid nitrogen to create the new surfaces and to prevent any possibility of phase deformation during the fracturing process. The TPC-ET phase was then preferentially extracted by immersion of the fractured surface into boiling dimethyl sulfoxide (DMSO) for about 20 min. The samples were later dried in a vacuum oven at 40 °C for 12 h to eliminate contamination by the solvent. The dried surfaces were gold-coated before they were imaged by scanning electron microscopy (SEM). From the SEM micrographs, the size of rubber domains dispersed in a copolyester (TPC-ET) matrix was determined in terms of the number-average (D_n) domain diameters using Equation (1) [40]:

$$D_n = \frac{\sum N_i D_i}{\sum N_i} \quad (1)$$

where N_i is the number of particles with the diameter D_i .

2.4.4. Dynamic properties

Dynamic properties in terms of storage and loss moduli, along with complex viscosity, were characterized using a moving die processability tester, model RheoTech MDPT, Tech Pro Inc., (Cuyahoga Falls, USA). Frequency sweeps were conducted over the frequency range from 0.1 to 158 rad/s at 3% strain amplitude and 180 °C according to ASTM D6601.

3. Results and discussion

3.1. Influence of vulcanization system choice on properties of MNR compounds

3.1.1. Curing properties of MNR compounds

Figure 1 shows cure curves or torque-time curves of MNR compounds with various vulcanization systems. It is seen that different vulcanization systems exhibit different cure characteristics. That is, the peroxide and mixed sulfur-peroxide systems show a plateau curing curve with almost constant torque at the final vulcanization state. This indicates the optimum cure or equilibrium in rubber vulcanization. On the other hand, the sulfur-cured system exhibits slight reversion by marginally dropping torque around the testing time of 20 min. This arises from the breakdown of weak newly formed linkages, such as disulfidic ($-C-S-S-C-$) and polysulfidic ($-C-S_x-C-$) linkages, that a vulnerable to elevated temperature and high shear. In addition, the phenolic curing system shows different cure behavior by increasing torque as testing time increases or marching cure behavior. Table 3 summarizes the cure properties in terms of minimum and maximum torques, torque difference, scorch time, cure time, and cure rate index (CRI) for the MNR compounds with the various vulcanization systems. It can be seen that the peroxide-cured case has the highest maximum torque and torque difference

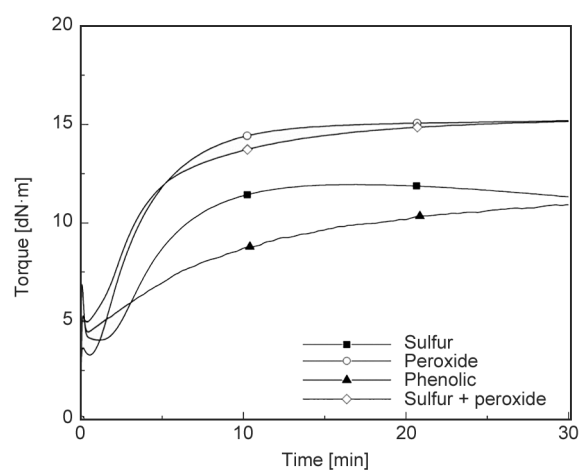


Figure 1. Torque-time curves of MNR compounds prepared with various vulcanization systems.

Table 3. Cure properties in terms of minimum and maximum torques, torque difference, scorch time, cure time, and cure rate index (CRI) for the MNR compounds prepared with various vulcanization systems.

Vulcanization system	M_L [dN·m]	M_H [dN·m]	$M_H - M_L$ [dN·m]	t_{s1} [min]	t_{c90} [min]	CRI [min ⁻¹]
Sulfur	4.04	11.95	7.91	2.31	9.09	14.75
Peroxide	3.27	15.44	12.77	1.16	9.20	12.44
Phenolic	4.77	11.56	6.79	2.44	28.49	3.84
Mixed sulfur-peroxide	4.95	15.33	10.38	1.16	13.42	8.16

among the tested vulcanization systems, whose rank order was peroxide > mixed sulfur-peroxide > sulfur > phenolic cured system. This is due to peroxide curing generating comparatively stronger carbon-carbon bonds between the rubber molecules relative to the other types of new linkages induced by the other vulcanization systems. On the other hand, the phenolic system gave the least maximum torque and torque difference. This may be due to slow reactions that formed the Chroman ring structures between MNR and dimethylol phenolic resin with active hydroxymethyl (methylol) groups, and this gave rise to a low crosslink density [41]. A proposed reaction mechanism is shown in Figure 2. It can be seen that the hydroxyl and methylol groups in phenolic molecules undergo reactions with unsaturation in MNR molecules to form Chroman rings as the bridge links between rubber molecules or to form crosslinks. Therefore, the slow crosslinking reaction rate of phenolic curing is obvious due to the molecular rearrangement to form Chroman rings and also due to the low level of unsaturation in MNR molecules. This is also reflected in the lowest cure rate index (CRI) and the longest scorch and cure times with the lowest maximum torque and torque difference (Table 3).

In Table 3, it can also be seen that the MNR compounds with sulfur and phenolic vulcanization systems show longer scorch time or improved scorch safety. Therefore, these two vulcanization systems may be suitable for preparing dynamically cured MNR/TPC-ET blends due to the long enough time for transformation from the co-continuous structure of MNR/TPC-ET simple blend to large vulcanized rubber particles and eventually, the dispersed micron-sized vulcanized rubber domains in the TPC-ET matrix.

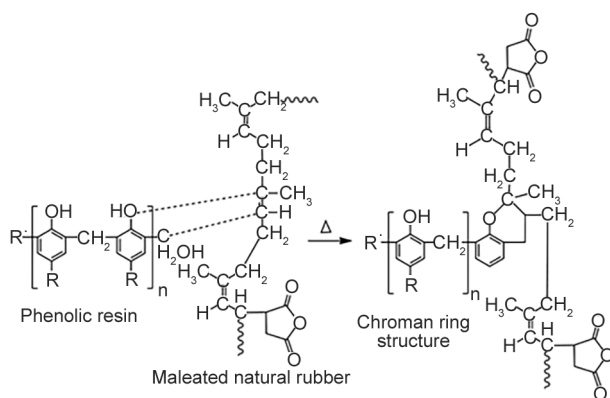


Figure 2. A proposed reaction mechanism of phenolic resin and maleated natural rubber.

3.1.2. Mechanical properties of MNR compounds

Figure 3 shows stress-strain behaviors of the MNR vulcanizates with various vulcanization systems. It can be seen that Young's modulus (*i.e.*, the initial slope of the curve), which reflects the stiffness of the material, had the order peroxide > phenolic > mixed sulfur-peroxide > sulfur by vulcanization system. This matches the trend in 100% moduli of the MNR vulcanizates based on static vulcanization with peroxide, phenolic, mixed sulfur-peroxide, and sulfur curing systems, which are 0.84, 0.55, 0.34, and 0.32 MPa, respectively. Furthermore, the area underneath the stress-strain curve, which indicates the toughness of the material, has the same trend as Young's modulus and 100% modulus. This is attributed to the peroxide curing system generating chemical crosslinks that consist mainly of carbon-carbon bonds ($-C-C-$ linkages) with higher bonding energy (about 347 kJ/mol) while the sulfur curing system gives weaker chemical bonds of mono-sulfidic ($-C-S-C-$, 301 kJ/mol), di-sulfidic ($-C-S-S-C-$, 271.7 kJ/mol), and poly-sulfidic types ($-C-S_x-C-$, < 271.7 kJ/mol) [42]. An illustration of the different types of crosslinks is shown in Figure 4. Furthermore, the phenolic curing system links rubber molecules by strong structures of phenolic resin, as indicated in Figure 2 and Figure 4d. This causes the phenolic-cured MNR vulcanizate to have slightly higher moduli than the ones prepared with mixed sulfur-peroxide and sulfur vulcanization systems.

Table 4 shows tensile properties (*i.e.*, tensile strength and elongation at break) and mechanical properties in terms of tension set and hardness (Shore A) of the MNR vulcanizates prepared with various vulcanization systems. It can be seen that tensile strength and

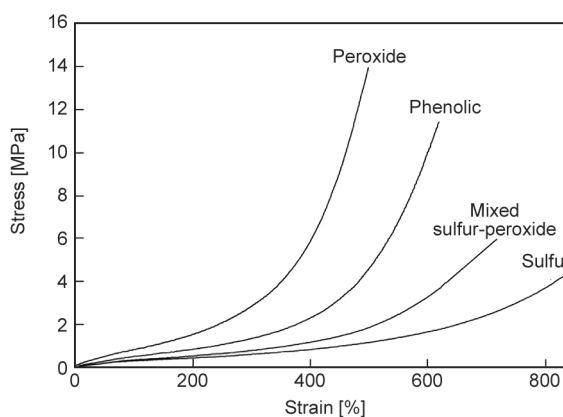


Figure 3. Stress-strain behaviors of MNR vulcanizates prepared with various vulcanization systems.

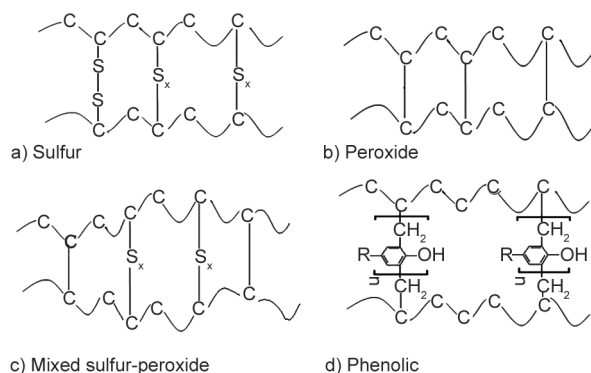


Figure 4. Representative models showing different types of crosslinks formed in a) sulfur, b) peroxide, c) mixed sulfur-peroxide, and d) phenolic cured systems.

hardness have similar trends as moduli and toughness in Figure 3. That is, these properties ranked as peroxide > phenolic > mixed sulfur-peroxide > sulfur vulcanization systems. This is again due to different bonding energies and structures of crosslinks from the alternative vulcanization systems. In Table 4, it is also seen that the highest elongation at break ($EB \cong 834\%$) was for the MNR vulcanizate with the sulfur curing system, while the peroxide system provided the lowest EB (499%). The phenolic and mixed sulfur-peroxide systems showed intermediate elongations at the break, at 618 and 678%, respectively. This may be due to the sulfur system giving di- and poly-sulfidic linkages with high elasticity, as indicated by the lowest tension set (0.5% in Table 4). However, the peroxide system with mainly $-C-C-$ linkages gave the lowest elastic properties, indicated by the highest tension set at 2.0% (Table 4). Furthermore, the phenolic and mixed sulfur-peroxide systems gave an intermediate tension set at 1.0%, which corresponds to the intermediate elongation at break as compared with the EBs of the MNR vulcanizates based on sulfur and peroxide curing (Table 4).

3.1.3. Dynamic mechanical properties of MNR compounds

Figure 5 shows the storage modulus as a function of oscillation frequency for the MNR compounds

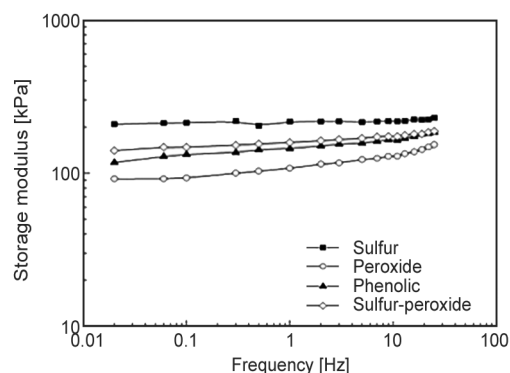


Figure 5. Storage modulus as a function of oscillation frequency for the MNR compounds prepared with various vulcanization systems.

prepared with various vulcanization systems. It can be seen that the storage modulus slightly increases with frequency due to a shorter time available for molecular relaxations. The storage or elastic modulus typically represents the amount of energy stored in a tested sample. In Figure 5, it can be seen that the storage modulus at a given frequency had the order sulfur > mixed sulfur-peroxide > phenolic > peroxide by the vulcanization system. Therefore, the MNR vulcanizates with sulfur-containing curing systems (*i.e.*, sulfur or mixed sulfur-peroxide vulcanization system) showed higher elastic moduli with more energy stored than the MNR prepared with phenolic or peroxide curing system. This is again due to the higher elasticity of sulfidic linkages, which corresponds to lower $\tan \delta$ at a given oscillation frequency for the MNR compounds cured with sulfur or mixed sulfur-peroxide curing system, as shown in Figure 6. It is noted that $\tan \delta$ is the damping factor or loss factor defined as the ratio of the moduli (*i.e.*, loss modulus, G'' /storage modulus, G'). Typically, $\tan \delta$ indicates the relative degree of energy dissipation or damping by the material and hence rubber elasticity. In Figure 6, the MNR vulcanizate based on sulfur curing shows the lowest $\tan \delta$ or damping factor, which indicates the highest rubber elasticity. Also, the trend of $\tan \delta$ is reversed from that of the storage modulus (Figure 5): sulfur < mixed sulfur-peroxide < phenolic

Table 4. Tensile properties (*i.e.*, tensile strength and elongation at break) together with tension set and hardness (Shore A) for the MNR vulcanizates prepared with various vulcanization systems.

Vulcanization system	Tensile strength [MPa]	Elongation at break [%]	Tension set [%]	Hardness [Shore A]
Sulfur	4.32±0.01	834±9	0.5±0.01	22.0±1.0
Peroxide	13.98±0.03	499±8	2.0±0.03	34.0±1.0
Phenolic	11.48±0.11	618±8	1.0±0.02	29.0±1.0
Mixed sulfur-peroxide	5.26±0.02	678±6	1.0±0.03	24.0±1.0

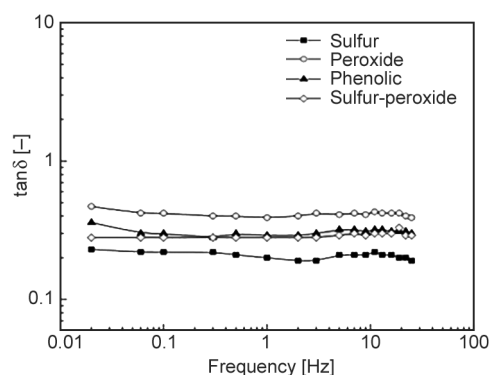


Figure 6. $\tan \delta$ as a function of oscillation frequency for the MNR compounds prepared with various vulcanization systems.

< peroxide by vulcanization system. Therefore, the sulfur-containing systems (*i.e.*, sulfur or mixed sulfur-peroxide vulcanization system) provide the most energy storage with the highest rubber elasticity, while the MNR with peroxide curing system has the lowest elasticity with the highest energy dissipation. On the other hand, the phenolic-cured MNR vulcanize shows intermediate moduli and loss factor.

3.2. Influence of vulcanization system choice on properties of dynamically cured MNR/TPC-ET blends

3.2.1. Time profiles of mixing torque and temperature

Figure 7 shows time profiles of torque and temperature during the mixing of the dynamically cured MNR/TPC-ET blends with various vulcanization systems. It can be seen that the mixing torque-time curve showed three peak locations, with the first one at the initial mixing when TPC-ET was added to the mixing chamber. The second peak at about the mixing time of 2 min occurs after incorporating the MNR

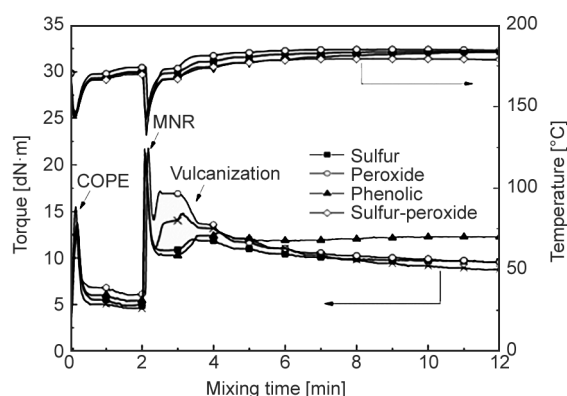


Figure 7. Mixing torque-time and mixing temperature-time curves for the dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems.

compound that abruptly increased the mixing torque, which then immediately decreased. The third peak (*i.e.*, dynamic vulcanization peak) has varying heights, locations, and the area underneath the peak, due to the differences in the nature of dynamic vulcanization based on the choice of curing system. After the addition of MNR compounds, the MNR/TPC-ET blend is forced to transform from a co-continuous phase structure of a simple blend characteristic to separated vulcanizing rubber domains that are dispersed TPC-ET matrix during dynamic vulcanization [43]. The final blend morphology of the dynamically cured MNR/TPC-ET blend is a micron-sized dispersion of vulcanized MNR domains in the TPC-ET matrix. In Figure 7, it is seen that the peak height and area underneath the third peak can be ordered as peroxide > mixed sulfur-peroxide > phenolic > sulfur by the vulcanization system. We anticipate that the height and area underneath the third peak directly relate to the degree of vulcanization and the strength of crosslinks formed in the rubber phase. This is in good agreement with the maximum torque (Table 3), tensile strength, and hardness (Table 4), together with moduli and toughness (Figure 3) of the MNR compounds with different static vulcanization systems. However, the torque difference of the MNR compound based on static vulcanization has a similar trend in peak height and area under the third peak, but there is a discrepancy in delta torques of the phenolic and sulfur cured systems at 6.79 and 7.91 dN·m, respectively (Table 3). This may be attributed to the rubber phase in the dynamically cured MNR/TPC-ET blend with the sulfur curing system having a higher crosslink density than with the phenolic curing system. In Figure 7, the third peak location with different vulcanization systems corresponds to the scorch time (t_{s1}), or time till the onset of vulcanization, which is the time until one torque unit rise above the minimum torque. That is, the peroxide and mixed sulfur-peroxide curing systems gave the lowest scorch time of about 1.16 min (Table 3). It corresponds to the earliest peak location in dynamic vulcanization during mixing at about 3 min. On the other hand, the sulfur and phenolic curing systems gave scorch times of 2.31 and 2.44 min, which correspond to third peak locations in dynamic mixing at about 3.3 and 3.4 min, respectively. It is therefore concluded that the phenolic and sulfur curing systems offer improved process safety against premature vulcanization of the dynamically cured MNR/TPC-ET blends.

In Figure 7, it can be seen that the final mixing torque has a different trend than the area under the curve and the third peak location and can be ordered as phenolic > peroxide \cong sulfur > mixed sulfur-peroxide by curing system. It is noted that the final mixing torque should have a close relation to the torque difference or the maximum torque of the statically cured MNR compounds (Table 3). However, the discrepancy may arise from the different shear and heat treatments in static (Table 3) and dynamic vulcanization (Figure 7). That is, the 12 min mixing time is optimal at 170 °C for dynamic vulcanization of the MNR/TPC-ET blends with the phenolic curing system to reach full vulcanization, as a plateau mixing torque vs. time curve is seen (Figure 7). However, in the static vulcanization of the MNR compound with the phenolic curing system (Figure 1) at the final testing time of 30 min, marching cure behavior with a steady increase in torque still exists. It means more time is needed to cure the MNR vulcanizate in static curing conditions fully. In Figure 7, other vulcanization systems (apart from the phenolic curing system) show a gradually decreasing trend of the mixing torque with time. This may be due to the destruction of some crosslinks after full vulcanization was reached. Therefore, the properties of the static and dynamic curing of MNR may be different due to different network characteristics and crosslink structures in the MNR vulcanizate and the MNR/TPC-ET blend. In Figure 7, it is also seen that the mixing temperature decreases after adding TPC-ET at the start of the mixing process and after incorporating the MNR compound at the mixing time of 2 min. After continued mixing with a rotor speed of 60 rpm, the mixing temperature is marginally increased due to shear heating and the exothermic reaction of rubber vulcanization [44].

3.2.2. Mechanical and morphological properties

Figure 8 shows stress-strain curves of dynamically cured MNR/TPC-ET blends prepared with different vulcanization systems. It is seen that Young's modulus (*i.e.*, initial slope in the linear region of the curves) of the blends can be ordered as phenolic > sulfur \cong peroxide > mixed sulfur-peroxide by curing system. This corresponds to the trend of final mixing torques of dynamic vulcanization (Figure 7) where the blend with the phenolic system shows the highest. Still, the mixed sulfur-peroxide cured system shows the lowest final mixing torque and hence

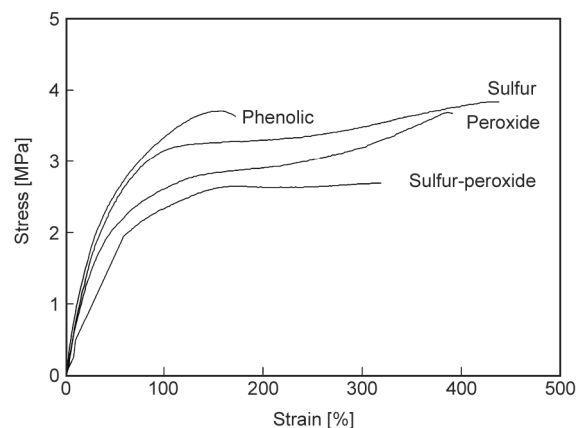


Figure 8. Stress-strain curves of dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems.

lowest Young's modulus and stiffness. This also corresponds well to the morphological properties (SEM micrographs in Figure 9) and to average sizes of vulcanized MNR domains in the dynamically cured MNR/TPC-ET blends with various vulcanization systems, shown in Table 5. It can be seen that the smallest vulcanized rubber domains (about 1.8 μm) are found in the dynamically cured MNR/TPC-ET blend with the sulfur curing system (Figure 9a) and the largest domains (about 5.0 μm) are in the blend with the mixed sulfur-peroxide curing system (Figure 9d). Furthermore, the peroxide and phenolic curing systems show intermediate vulcanized rubber domain sizes at 2.5 and 3.5 μm (Figures 9b and 9c, respectively, and Table 5). It is noted that the smaller rubber domains result in less interfacial tension but, more interfacial area and interfacial adhesion, causing enhanced strength and other related properties of the dynamically cured MNR/TPC-ET blends.

Figure 10 shows the tensile strength of dynamically cured MNR/TPC-ET blends with different vulcanization systems before and after aging. It can be seen that the tensile strength or strength at the break of the blend is in good agreement with the trend of Young's moduli (Figure 8) and with the average domain sizes of the vulcanized rubber particles (Table 5 and Figure 9). That is, the MNR/TPC-ET TPV with sulfur curing system has the highest tensile strength with the smallest vulcanized MNR domains, while the TPV with mixed sulfur-peroxide vulcanization system shows the lowest tensile strength with the largest rubber domains. The MNR/TPC-ET TPVs with peroxide and phenolic curing systems have intermediate tensile strengths and sizes of vulcanized MNR domains. In Figure 10, it is clear that the tensile

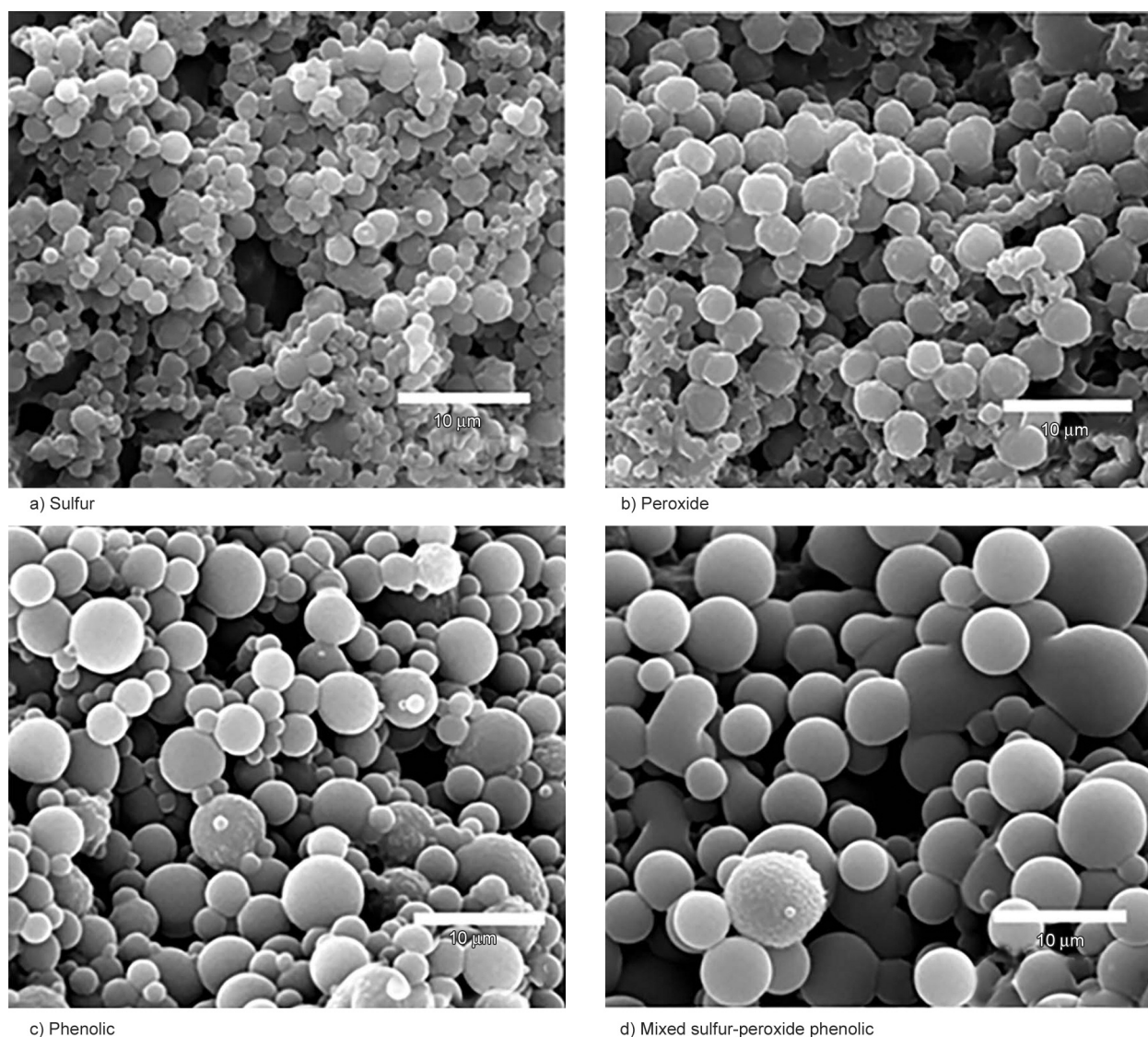


Figure 9. SEM micrographs of dynamically cured MNR/TPC-ET blends with various vulcanization systems. a) sulfur, b) peroxide, c) phenolic, and d) mixed sulfur-peroxide phenolic

strength of all TPVs increases after prolonged heat aging at 100 °C (for 22 h) tested according to ASTM D573. This may be due to an increase in newly formed crosslinks in the rubber vulcanizate, with increased crosslink density after the heat treatment. Also, the heat treatment may improve the interfacial adhesion between TPC-ET and MNR, with a proposed reaction shown in Figure 11. It is seen that a

Table 5. Average particle size of vulcanized rubber domains in the dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems.

Vulcanization system	Vulcanized rubber domain size [µm]
Sulfur	1.8±0.19
Peroxide	2.5±0.19
Phenolic	3.5±0.07
Mixed sulfur-peroxide	5.0±0.11

chemical interaction between MNR with phenolic curing system and TPC-ET molecules at interfacial areas of MNR/TPC-ET TPV may occur via hydrogen

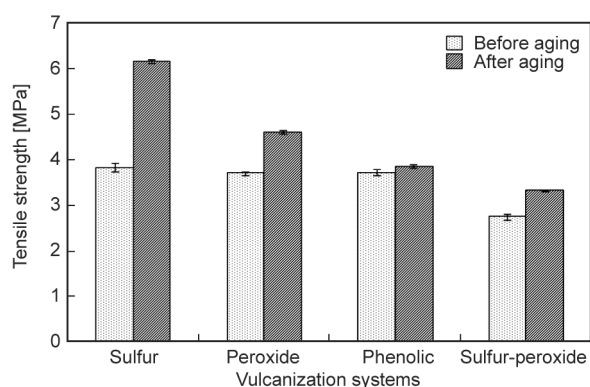


Figure 10. Tensile strength of dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems, before and after aging.

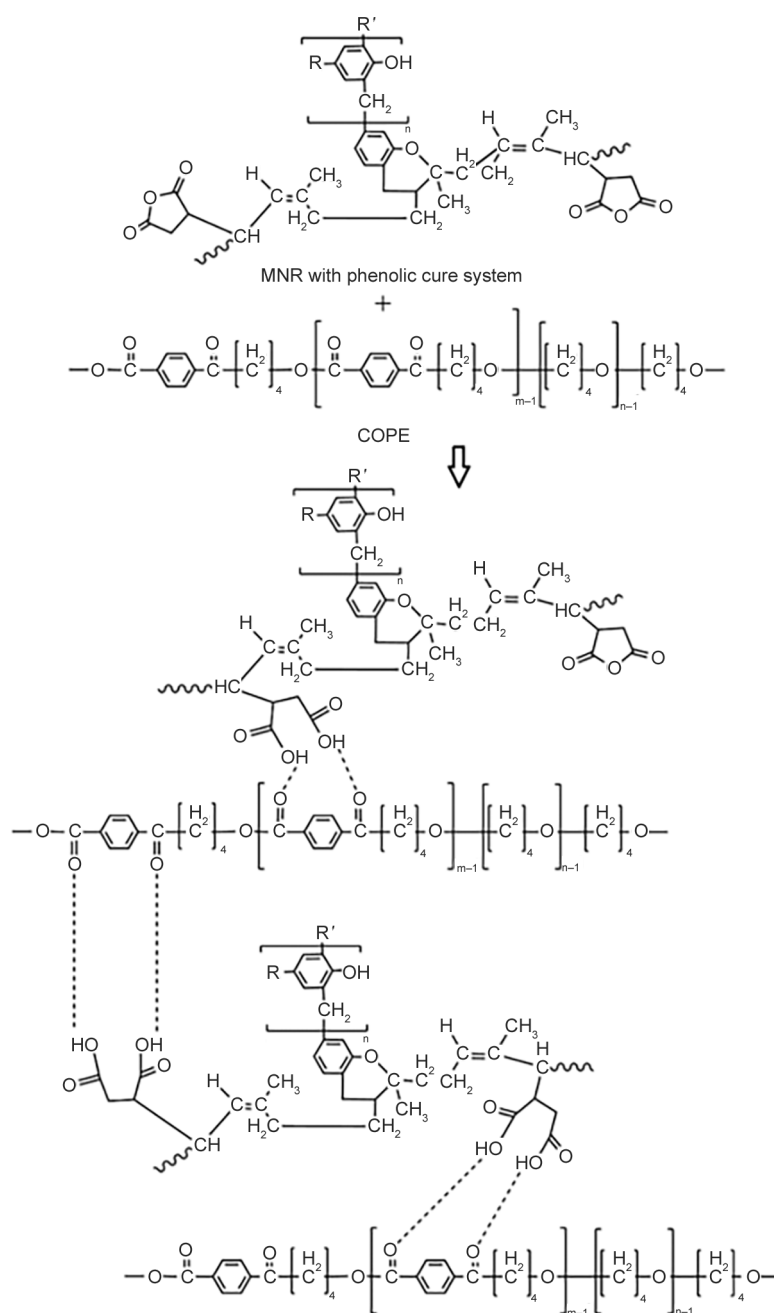


Figure 11. A possible chemical interaction via H-bonding of MNR with phenolic curing system and TPC-ET molecules at interfacial areas of MNR/TPC-ET TPV.

bonds. This is in agreement with the aging properties of NR composites with different sulfur curing systems, in which cases the overall crosslink densities increased with aging time and temperature [45]. In this work, various MNR/TPC-ET TPVs were aged by conditioning at 100 °C for 22 h in a multi-cell aging oven, Elastocon AB (Brämhult, Sweden). Likewise, under this static heat treatment, the rubber component with various vulcanization systems in the MNR/TPC-ET TPVs has the capacity to create newly formed crosslinks from the remaining curative residues and hence causes increases in the strength

properties. In a sulfur-cured case, some curatives such as free sulfur, cure accelerators, and their residues remained in the cured rubber compound. It is claimed that free sulfur is effective in increasing crosslink density during thermal aging [45].

This causes the MNR/TPC-ET TPV with a conventional sulfur curing system to have a prominent increase in crosslink density and hence in tensile strength properties after aging. Likewise, with the peroxide curing, the remaining peroxide residues are still reactive under aging and can react with MNR to form the new –C–C– crosslinks, increasing

the crosslink density and hence tensile strength, but this is at a lower level compared to the sulfur curing system. Furthermore, in TPV with phenolic curing, the least increased tensile strength is seen after heat aging. This may be due to the reaction mechanism to form Chroman rings that would need a longer time (Table 3 and Figure 7) and possibly also more energy. Also, steric hindrances to Chroman rings may retard the formation of the rubber polymer network. In Figure 10, it is also seen that the mixed sulfur-peroxide curing system also gave a higher tensile after aging due to the reactions of sulfur and peroxide curing agents.

Figure 12 shows elongation at break of the dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems before and after aging. It can be seen that the elongation at break after aging of all TPVs also was slightly higher than before aging. This might be for the same reason, namely that all the vulcanization systems induced crosslinking with remnants of the crosslinking agents during static heat treatment of MNR, contributing to higher elastic properties. In addition, the elongation at break of various TPVs based on the different vulcanization systems has a similar trend with tensile strength, but the reverse trend is seen in the mixed sulfur-peroxide, and the phenolic cured system. This may be due to the constraint of Chroman rings in crosslinks of the phenolic cured TPV (Figure 2) and is in good agreement with Young's modulus and hence stiffness (Figure 8). This contributes to the rigidity of the crosslinked rubber and hence the MNR/TPC-ET TPV. Therefore, the phenolic cured material has the highest stiffness (as indicated by the highest Young's modulus in Figure 8), together with large-sized vulcanized rubber

domains (Figure 9). The large vulcanized rubber particles may relate to the low content of Chroman rings in MNR during dynamic vulcanization and also to short scorch time, leading to low viscosity, shear and elongation being able to break down the vulcanizing MNR domains. This results in a lower crosslink density, as evidenced by the lowest torque difference (Table 3). Furthermore, the lower content of Chroman rings also results in a lesser interfacial surface area, weaker interfacial interactions between MNR and TPC-ET and hence larger vulcanized MNR domains (Figure 9).

Figure 13 shows the tension set and hardness (Shore A) of dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems. It is noted that the tensile set (or tension set) testing of a rubber or thermoplastic elastomer evaluates the residual elongation of a test sample after being stretched and allowed to relax in a specified manner. This elongation consists of both permanent and recoverable components, thus, the tension set is used to measure the ability of a rubber sample to retain its elastic properties after extension. Therefore, a lower tension set means higher elastic properties of the material. In Figure 13, it is clear that the elastic properties in terms of tension set correspond to the trend of elongation at break as sulfur > peroxide > mixed sulfur-peroxide > phenolic by vulcanization system. Therefore, the phenolic and peroxide-cured MNR/TPC-ET TPVs with rigid crosslinks of Chroman rings and $-C-C-$ linkages (Figure 4) have more rigidity and stiffness but less elasticity. However, the sulfidic linkages are more flexible with higher extensibility and elasticity (Figure 8). These also correspond to higher hardness of the phenolic and peroxide cured

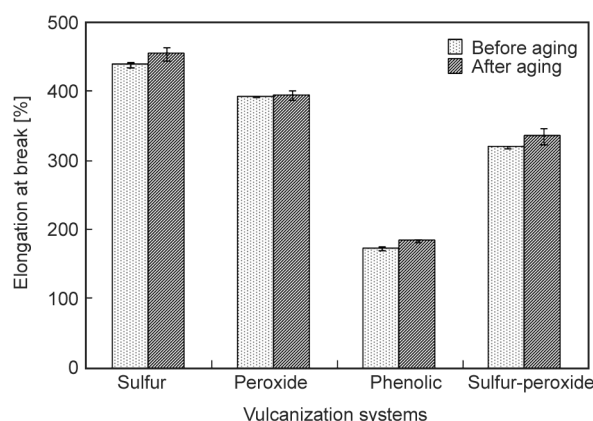


Figure 12. Elongation at break of dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems, before and after aging.

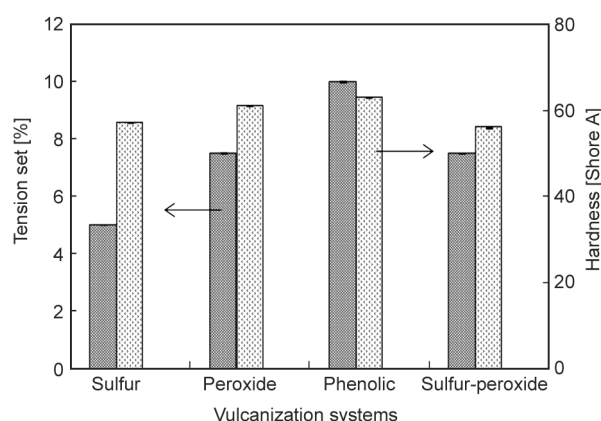


Figure 13. Tension set and hardness (Shore A) of dynamically cured MNR/TPC-ET blends prepared with various vulcanization systems.

MNR/TPC-ET TPVs than for the sulfur and mixed sulfur-peroxide cured TPVs.

4. Conclusions

Maleated natural rubber (MNR) was in-house prepared and compounded with four alternative vulcanization systems, *i.e.*, sulfur, peroxide, phenolic, and mixed sulfur-peroxide systems. We found that the peroxide and mixed sulfur-peroxide systems showed a plateau curing curve with an equilibrium state, while the sulfur system exhibited a slight reversion due to the breakdown of weak sulfidic linkages. Also, the phenolic system gives a marching cure. Dynamically cured MNR/TPC-ET blends using the four alternative MNR compounds were then prepared and characterized. It was found that the height and area underneath the third peak for dynamic vulcanization in the mixing torque *vs.* time curve relates to the degree of vulcanization and strength of cross-links, which can be ordered as peroxide > mixed sulfur-peroxide > phenolic > sulfur by the vulcanization system. These are in good agreement with maximum torque, tensile strength, hardness, moduli, and toughness (the area underneath the stress-strain curve) for the MNR compounds prepared with static vulcanization. The location of the dynamic vulcanization peak also corresponds to the scorch time (t_{s1}) of the static vulcanization, where the peroxide and mixed sulfur-peroxide curing systems gave the shortest scorch time with the earliest peak location at a mixing time of about 3 min. The sulfur and phenolic systems had scorch times of 2.31 and 2.44 min and peak locations at 3.3 and 3.4 min, respectively. Therefore, the phenolic and sulfur systems offer more process safety against premature reactions in dynamically cured MNR/TPC-ET blends. It was also found that the TPV with sulfur curing system had mono-, di- and poly-sulfidic linkages in the rubber networks giving the smallest vulcanized rubber domains dispersed in the TPC-ET matrix, causing the highest interfacial adhesion and hence tensile strength, elongation at break, storage modulus, and rubber elasticity in terms of the lowest tension set and $\tan \delta$ (in dynamic test). However, the phenolic cured TPV shows the highest stiffness, Young's modulus (*i.e.*, the highest slope at the initial part of the stress-strain curve), and large vulcanized rubber domains. This may be related to low contents of Chroman rings crosslinking the MNR networks, causing lower surface area and interfacial

interaction between MNR and TPC-ET phases. The mixed sulfur-peroxide and peroxide curing systems showed intermediate tension set, $\tan \delta$, and elongation at break. Furthermore, the tensile strength and elongation at break increased in all cases after aging by heat treatment. This is due to the continued curing reactions of MNR during heat treatment. The phenolic-cured TPV showed the least change in tensile properties from aging, due to slow reactions that form Chroman rings. Therefore, it is concluded that the sulfur-cured system offers the best overall properties of the MNR/TPC-ET TPV.

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