Assessment Degradation of Natural Rubber by Moving Die Processability Test and FTIR Spectroscopy

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ABSTRACT: Thermal and mechanical degradation of natural rubber (NR) mixed with N-(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine (6PPD), polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline (TMQ), and 50/50 weight basis mixture under high temperature and shearing conditions were investigated using a moving die processability test and FTIR spectroscopy. Relationship between dynamic properties in terms of tan δ value and chemical changes of NR molecules during degradation were correlated. The results indicated that the NR mixed with antioxidants caused decreased level of chain scission and oxidative degradation. The 6PPD provided better protection of NR against degradation at elevated temperature than TMQ. Furthermore, it was found that a prolonged mixing time caused more pronounced oxidative degradation on NR molecules than increased mixing temperature. The antioxidative capability of those antioxidants on NR was ordered based on their effectiveness as follows: 6PPD > 6PPD mixed with TMQ > TMQ. It was also found that the moving die processability test and FTIR spectroscopy are efficient routes to estimate the oxidative degradation of NR molecules. Therefore, the techniques could be applied to assess or compare antioxidative capability of various types and amounts of antioxidants used in the rubber formulation within a reasonable testing time. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1702–1709, 2010

Key words: natural rubber; oxidative degradation; dynamic properties; tan δ; FTIR, TMQ, 6PPD

INTRODUCTION

The susceptibility of natural rubber to degradation is one of the main problem encountered in the rubber industry. Unsaturation in the rubber chains makes the materials more susceptible to heat because the energy required to break π-bonds in the C=C linkages to form active radicals is relatively low. This causes a marked deterioration in the mechanical properties and a decrease of molecular weight. Oxidation process causes the main degradation phenomenon (i.e., oxidative degradation) of the natural rubber molecules. It generally occurs quite slowly at ambient temperatures, but is of greater consequence with increasing temperatures.[1] Oxidative degradation is free radical processes which can be initiated by various modes. These include thermal, mechanical, photochemical, radiation chemical, biological, and chemical degradations. Generally, the degradation initiates by breaking carbon–hydrogen and carbon–carbon bonds along the backbone chain. Consequently, unstable carbon radicals (R•) are formed. These radicals react readily with oxygen to form peroxy radicals (ROO•) which consequently abstract labile hydrogen atoms from other polymer molecules to form a hydroperoxide (ROOH) and another carbon radical to propagate the cycle. The process becomes autocatalytic when the hydroperoxide decomposes into two types of radicals: alkoxy (RO•) and hydroxy (HO•) radicals.[2] These reactions lead to chain scission and/or increased crosslinking, depending on the type or characteristics of the rubber and the reaction condition. In natural rubber molecules, the presence of methyl groups in the side chain markedly causes a formation of tertiary hydroperoxides. This leads to severe chain scission at high temperature.[3,4] Mastication of NR at high temperature in an internal mixer has been known phenomenon for main consequence to reduce bulk viscosity (i.e., Mooney viscosity) by oxidation, and scissions, of chains.[5,6] The rate of the oxidation process of rubber molecules is retarded or suppressed by incorporation of antioxidants which can be used to prolong the service life of the rubber vulcanizates. Generally, antioxidant molecules are capable of reacting with peroxides to form stable end groups, or with free radicals to suppress oxidative degradation process. The most common antioxidants used in
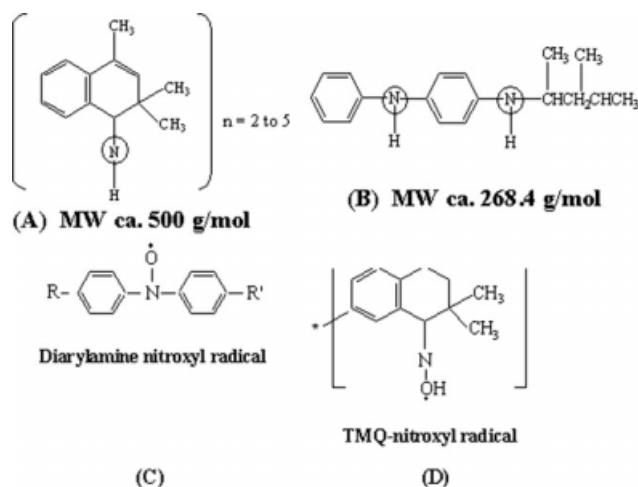
Figure 1 Molecular structures of (A) TMQ (polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline), (B) 6PPD (*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine), (C) diarylamine nitroxyl radical, and (D) TMQ-nitroxyl radical.

the rubber industry are amine and amine derivative. This includes secondary aromatic amine, such as *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylene diamine, 6PPD and polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline, TMQ. 6PPD has been used as an antidegradant to protect rubber against ozone and oxygen as well as fatigue under static and dynamic conditions, whereas TMQ has been an excellent antioxidant and long lasting heat stabilizer because of its higher molecular weight.

Degradation of elastomeric materials have been characterized using various methods. These include NMR spectroscopy,[3] IR spectroscopy,[7,8] DMA,[4] DSC,[9] TGA,[10–12] and oxygen uptake in the molecular structure of the rubber.[13] The FTIR technique has been extensively used to enable qualitative and quantitative analysis of the appearance/disappearance of functional groups such as carbonyl and hydroxyl groups in rubber molecules due to the oxidation process.[10,14] Thermo-oxidative degradation of polyisoprene (PI) rubber with different concentrations of 6PPD has been previously investigated using FTIR imaging technique.[7,8] Moving die processability tester is a dynamic mechanical rheological tester which is used with frequency or strain sweep modes. Melt behavior dependant molecular characteristics, such as viscosity or molecular weight have been investigated and correlated.[15,16] It is well established that viscoelastic measurements provide information of the molecular parameters through their relationship with a structure. Thus, the dynamic properties directly reflect the changes of molecular parameters, such as molecular weight and molecular weight distribution (MWD). Therefore, a change in loss angle tangent (tan δ) which relate to a balance between the viscous and elastic behavior

in a polymer melt could indicate an increase of macromolecular mobility due to the chain scission of NR during degradation process.[4] In addition, FTIR spectroscopy could be used to analyze the chemical changes of elastomer molecules and the presence of degradation product such as aldehyde, ketone, alcohol, and ether groups from oxidative degradation.[8,10,12,17]

In this work, a moving die processability test was used to determine the loss tangent or damping factor (i.e., tan δ) and correlated to chemical changes of the natural rubber molecules based on FTIR characterization. The main aim was to determine a relationship between chemical and dynamic mechanical properties changes of the natural rubber molecules during an oxidative degradation process. Effect of antioxidant on the protection efficiency of the natural rubber was also investigated.

EXPERIMENTAL

Materials

The natural rubber used was an air-dried sheet (ADS), manufactured by a local factory operated by Khuan Pan Tae Farmer Cooperation (Phattalung, Thailand). Two types of antioxidants were used without purification: *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD) and polymerized 1,2-dihydro-2,2,4-trimethyl-quinoline (TMQ), manufactured by Flexsys N.V., Brussels, Belgium. The molecular structures of 6PPD and TMQ are shown in Figure 1. Acetone and toluene used for sample purification were manufactured by Lab Scan Ltd, Ireland.

Mixing of NR with antioxidant

Natural rubber rubber (i.e., ADS) was mixed with 6PPD and TMQ antioxidants using internal mixer, Brabender Plasticorder PLE 331 (Duisberg, Germany) with a rotor speed of 60 rpm, as per formulations shown in Table I. NR was first masticated for 1 min, antioxidant was then added and mixing was continued for 5 min at 160°C. In this work, the influence of mixing time after incorporation of antioxidant at 5 and 10 min at two different

TABLE I
Formulations of Natural Rubber Mixed with Antioxidants

Ingredients	Quantities (phr)			
	A_0	A_1	A_2	A_3
NR (ADS)	100	100	100	100
6PPD	–	4	–	2
TMQ	–	–	4	2

temperatures of 160 and 180°C was also studied. In the case of NR without antioxidant (A_0), the rubber was masticated using the same condition. The sample was later sheeted out and kept at room temperature for 24 h.

Moving die processability test

Dynamic properties under a frequency sweep were tested using a moving die processability tester (rheeoTECH MDPT, moving die precessibility tester, Tech Pro, Cuyahoga Falls, OH) equipped with conical-shaped dies which produces a uniform shear strain on the sample during deformation at a constant strain amplitude. Sample size of 4 to 6 cm^3 was loaded onto the lower die and then the upper die was closed to form a constant volume in a compression mold. The oscillating frequency was set in the range of 0.13 to 188.5 rad/s at a constant strain of 5% and 100°C. At this strain magnitude, a linear viscoelasticity of the material was observed.[16] The storage (G'), loss shear (G'') modulus and loss tangent, tan $\delta = G''/G'$ were characterized.

FTIR spectroscopy

The crude sample of 1.5 g was first dissolved in 50 mL of toluene. An excess amount of acetone was then added to precipitate the dissolved rubber. The precipitated-rubber product was again washed thoroughly with acetone and dried in a vacuum oven at 40°C for 24 h. A small amount ($\sim$0.3 g) of the dried product was later dissolved in 10 mL of toluene for film casting on a KBr disk. FTIR spectroscopy (Omnic ESP Magna-IR 560 Spectrometer, Nicolet, Nicolet Instrument Corporation, WI) at a resolution of 4 cm^{-1} with the spectral range of 4000–400 cm^{-1} was used to analyze the thin film of rubber.

Determination of viscosity average molecular weight

NR mixed with various types of antioxidants (Table I) were dissolved in tetrahydrofuran (THF) with a range of concentrations of 0.025 to 0.400 g/dL. The dilute solution of polymer was then filtered using Whatman filter paper number 1450−240 with fine porosity. Intrinsic viscosity, [η], was determined according to Huggins-Kraemer equation by mean of Ubbelohde-type capillary viscometer.[18] Viscosity average molecular weight ($\bar{M}_v$) was calculated via Mark–Houwink-Sakurada equation, as follows:

$$[\eta] = k\bar{M}_v^a \tag{1}$$

where [η] is intrinsic viscosity, $\bar{M}_v$ is viscosity average molecular weight, $k = 0.36 \times 10^{-4}$ dL/g, and $a = 0.92$.[17]

Thermogravimetric analysis (TGA)

Thermal decomposition behavior of 6PPD and TMQ without rubber were analyzed by thermogravimetric analysis (TGA) using TGA7 (Perkin Elmer). Approximately 10 mg of sample was heated with a heating rate of 10°C/min under O_2 atmosphere.

RESULTS AND DISCUSSION

Dynamic properties of NR during degradation

Figure 2 shows tan δ as a function of frequency of unmasticated and masticated NR without antioxidant at various mixing conditions. It is seen that the tan δ decreased with increasing frequencies. This is attributed to shortened time available for molecular relaxation at high-oscillating frequencies. This caused the dashpot components could not response to the stress in time. The tan δ at a given frequency of the unmasticated NR shows the lowest value. It can also be seen that the tan δ values increased with increasing mixing times and temperatures. Increasing tan δ values characterize an increase of loss modulus (i.e., tan $\delta = G''/G'$) which indicates increasing viscous response or decreasing of elastic response of the material. This corresponds to increasing in macromolecular mobility which was more difficult to recover, or snap-back as random coils as, the degradation proceeds due to an increase of chain scission of NR molecules. This phenomenon corresponds to decreasing of the Mooney viscosity of NR rapidly and continuously during high-temperature mastication.[6] With respect to the mesostructure of NR, mastication under high-temperature condition provoked a rapid degradation of microgel. This caused decreasing of the Mooney viscosity or in this case increasing of tan δ. In Figure 2, it is also seen that the NR masticated at 160°C for
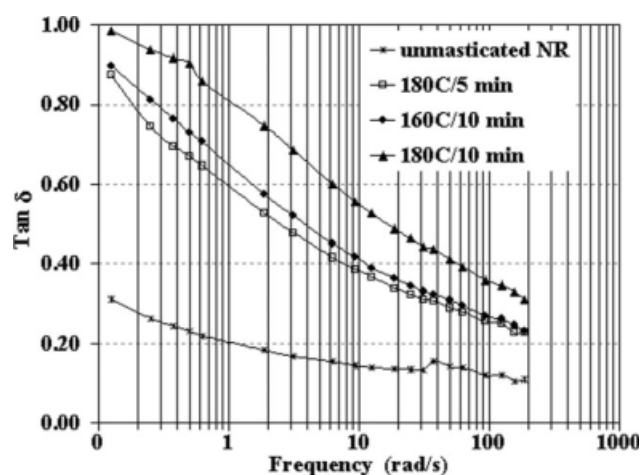

Figure 2 Tan δ as a function of frequency of NR without antioxidant at different mastication conditions.
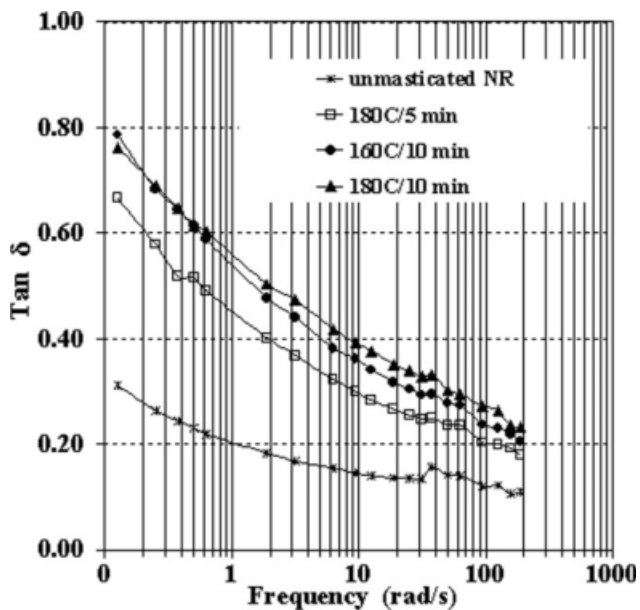
Figure 3 Tan δ as a function of frequency of NR mixed with 4 phr of 6PPD at different mixing conditions.

10 min shows higher tan δ value than the NR masticated at 180°C for 5 min. This reveals that longer mastication time even at lower temperature played significant role in level of degradation of NR molecules. This may be attributed to the concentration of macroalkyl radicals (R•) generated from the mechanical shearing during masticating of rubber.[19] The prolonged mastication at 160°C might generate higher concentrations of macroalkyl radicals than at 180°C but with a shorter period of shearing. As a result, greater chain scission and oxidative degradation occurred in the case of mastication at 160°C for 10 min.

In Figure 2, the highest tan δ values of the NR masticated without antioxidant was observed in the rubber with the longer mastication time at 180°C. This proves that severe mixing conditions in terms of higher temperature and longer mastication time caused a greater degree of oxidative degradation of the natural rubber molecules.

Figure 3 shows tan δ values as a function of frequency for the NR mixed with 4 phr of 6PPD antioxidant using various mixing conditions. It is again seen that the unmasticated NR showed lower value of tan δ than that of the NR mixed with 6PPD at various mixing conditions. It is also seen that the tan δ value of NR mixed with 6PPD increased with increasing mixing times and temperatures. The tan δ value of the NR mixed with 6PPD prepared at 160°C and 10 min was higher than that of the one prepared at 180°C and 5 min. This observation is the same as in the case of NR without antioxidant (Fig. 2). This proves that degradation of NR molecules with longer mixing time was more pronounced even at

lower temperature in the case of mixing NR with or without antioxidant. Incorporation of 6PPD in NR caused decreasing value of tan δ compared with the NR without antioxidant at the same mixing condition (i.e., 160°C and 10 min), as shown in Figure 4. This indicates a lower level of chain scission and oxidative degradation of NR molecules. This is attributed to the primary antioxidant (6PPD) which is sometimes called a chain breaking antioxidant or free radical trap and is capable of scavenging and destroying chain propagating species in the form of peroxy, alkoxy, and hydroxy radicals by donating active hydrogen atoms. The radicals are generally converted to inert by products, such as alcohol and water molecules. In addition, antioxidant radicals which are the products of the reaction are more stable. They do not abstract more hydrogen atoms from rubber molecules to create active free radicals. The reaction mechanism of protection against oxidative degradation of rubber molecules by aromatic amine antioxidant was reported elsewhere.[2]

Figure 5 shows complex viscosity as a function of oscillating frequency of NR mixed with 4 phr of 6PPD which was subjected to mechanical and thermal degradation at various mixing conditions. As may be expected, decreasing trend of the complex viscosity was observed with increasing frequency (or shear rate): shear-thinning behavior. The complex viscosity also decreased with increased mixing times and temperatures. Furthermore, it is seen that the complex viscosity of NR mixed at 160°C and 10 min was lower than that of the one mixed at 180°C and 5 min. This again confirms that the influence of mastication time plays a more significant role on the degree of degradation than temperature as discussed earlier. Therefore, it is concluded that increasing
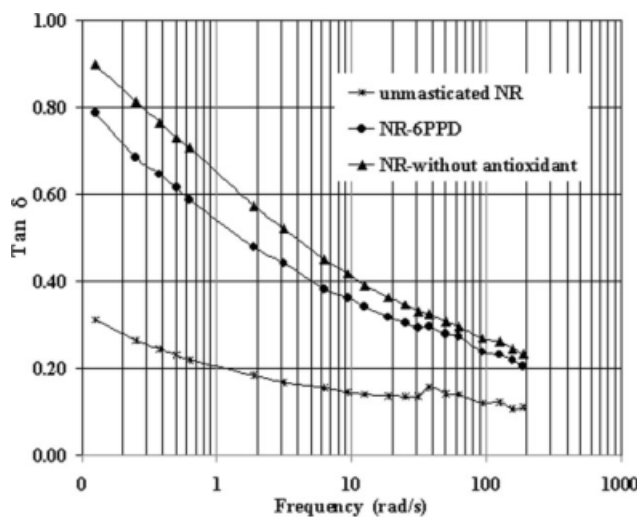

Figure 4 Tan δ as a function of frequency of unmasticated NR, NR without and mixed with 4 phr of 6PPD at 160°C and 10 min.
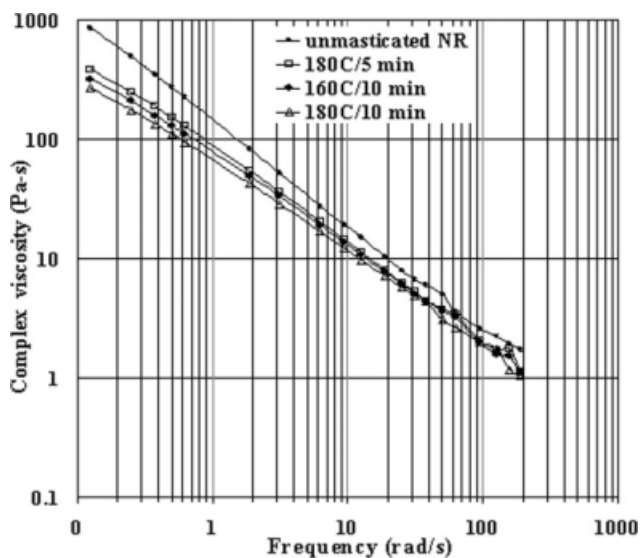
Figure 5 Complex viscosity as a function of frequency of NR mixed with 4 phr of 6PPD at different mixing conditions.

mixing temperature and time cause lower molecular weight due to oxidative degradation of NR molecules. This is proved by decreasing complex viscosity (Fig. 5) and viscosity average molecular weight ($\bar{M}_v$) of the rubber mixes, as shown in Figure 6. It can be seen that the unmasticated NR without antioxidant showed the highest viscosity average molecular weight, whereas the NR mixed with 6PPD at 180°C for 10 min exhibited the lowest value. The mixes prepared at 180°C for 5 min and 160°C for 10 min showed intermediate values with the last showing lowest molecular weight. It is clear that the complex viscosity correlates well with the molecular weight of the NR. Furthermore, the result corresponds to the trend of tan δ values at a given
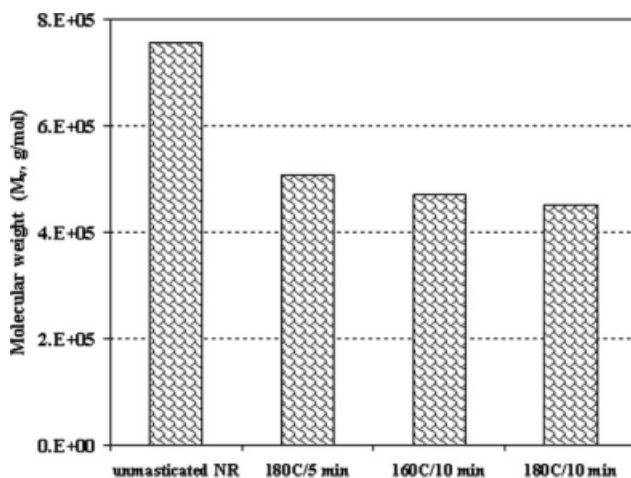
frequency (Fig. 3). Therefore, the progress of oxidative degradation of NR could be determined by means of tan δ value which correlated well with the value of complex viscosity and viscosity average molecular weight.

Effects of different types of antioxidants (i.e., 6PPD, TMQ, and mixture of both) on the evolution of tan δ values of NR mixed with 4 phr of antioxidants 180°C and 10 min are shown in Figure 7. The discrepancies in damping factor is more obvious in the low-frequency region rather than high-frequency one. This is attributed to at higher frequency range, shorter time is available for molecular relaxation. It can be seen that the NR mixed with 6PPD, TMQ, and mixture of 6PPD and TMQ showed lower tan δ values than that of the NR without antioxidant at the same mixing condition. Thus, incorporation of antioxidants caused an improvement of antidegradation. At low-oscillating frequencies, the effectiveness of each type of antioxidant was clearer. That is, it is clearly seen that the rubber mixed with 6PPD gave the lowest value of tan δ, followed by the mix with mixture of 6PPD and TMQ, and the mix with only TMQ, respectively. As discussed earlier, the addition of antioxidants to rubbers provides better protection against degradation by free radicals. However, efficiency of the antioxidants depends on various factors. One factor is the chemical structure that affects the ability of the antioxidant to trap peroxy and hydroxyl radicals and the catalytic action in hydroperoxide decomposition. In Figure 1, it is seen that 6PPD consists of two active hydrogen atoms per molecule, whereas TMQ contains only one. It is well established that more reactive hydrogen atoms cause higher efficiency of the antioxidant molecules to suppress or stop the oxidative degradation process. It has been well recognized that 6PPD in general is a
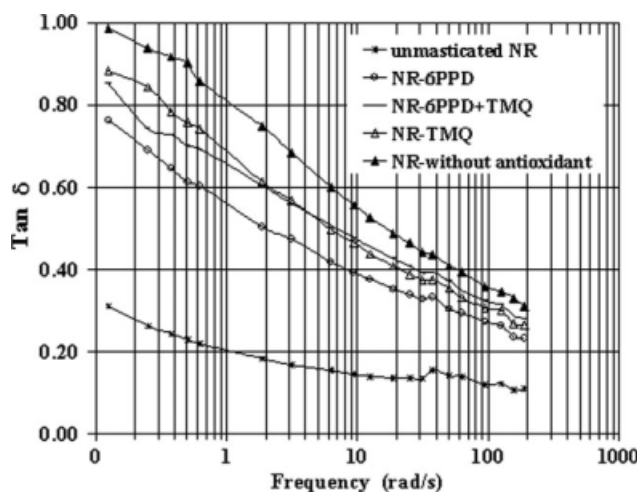

Figure 6 Viscosity average molecular weight ($\bar{M}_v$) of NR mixed with 4 phr of 6PPD at different mixing conditions.

Figure 7 Tan δ as a function of frequency of NR mixed with 4 phr of antioxidants 180°C and 10 min.
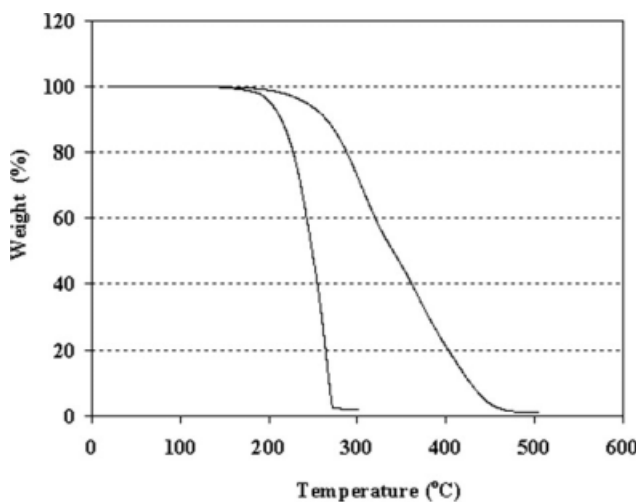
Figure 8 Thermogravimetric analysis of 6PPD and TMQ.

more efficient antioxidant than the TMQ.[20] In addition, nitroxyl radicals generated from amine typed antioxidant [i.e., in Fig. 1(C)] are able to destroy macroalkyl radicals (R•) generated from mechanical shearing action. The reactivity of diarylamine nitroxyl radicals is affected by delocalization, steric hindrance, and substitution. On the other hand, the TMQ-nitroxyl radical [Fig. 1(D)] is less efficient than the less hindered diarylamine nitroxyl radical found in 6PPD molecules.[20,21]

Solubility of the antioxidant in NR phase is another factor determining effectiveness of the antioxidant. Longer alkyl chains of 6PPD molecules cause higher solubility in NR.[7] Furthermore, according to thermogravimetric analysis in Figure 8, different weight loss and decomposition temperatures (T_d) of 6PPD and TMQ were observed. The 6PPD exhibited lower thermal stability than that of TMQ. However, the TMQ gives poorer oxidative protection of NR than that of 6PPD under a given shearing action and high temperature. This may be attributed to the TMQ having lower mobility in the rubber phase because of high-molecular weight.[1] In addition, the energy needed to withdraw the active hydrogen atom is relatively higher than required by the 6PPD counterpart.

In Figure 7, the rubber was subjected to more severe mixing conditions at 180°C and 10 min. However, the same trend of tan δ values was observed in NR mixed with 4 phr of antioxidants at 180°C, 5 min and 160°C, 10 min, as shown in Figure 9. Therefore, it is concluded that the rubber mixed with 6PPD gives the NR better protection against oxidative degradation in comparison with mixtures of 6PPD with TMQ as well as with TMQ alone, respectively. It is clear from these results that the difference in effectiveness of antioxidant in NR could be preliminarily assessed by determining tan δ value using moving die processability tester.

Figure 9 shows the tan δ values at the same testing frequency (i.e., 0.63 rad/s) of the NR mixed with different types of antioxidant and mixing conditions. It is clear that at the same mixing conditions, the NR mixed with 6PPD gave the lowest value of tan δ, followed by a mixture of 6PPD and TMQ, and only TMQ, respectively. The NR masticated without antioxidant gave the highest tan δ value which indicated severe oxidative degradation of the rubber molecules. Therefore, it is confirmed that addition of antioxidants resulted in significantly lower values of tan δ. In addition, NR with and without antioxidant at 160°C for 10 min showed higher tan δ values than that of the NR with and without antioxidant at 180°C for 5 min except for the NR mixed with TMQ. The last rubber mix showed higher tan δ values at 180°C for 5 min than at 160°C for 10 min. This might be attributed to TMQ losing its activity at elevated temperature. It is therefore concluded that the 6PPD gives the best protection for oxidative degradation of NR molecules at elevated temperatures and prolonged mastication followed by the use of a mixture of 6PPD with TMQ and lastly by only TMQ.

FTIR characterization

Figure 10 shows infrared absorption spectra of NR without antioxidant at different mastication conditions. It can be seen in Figure 10(A) that the intensity of infrared absorption peaks at 1710 cm^{-1}, which is assigned to stretching vibration of carbonyl groups, increased with increasing mastication times and temperatures. This indicates a certain degree of oxidative degradation occurred in NR molecules during mastication. In addition, it is seen that increasing in carbonyl species in the NR molecules expense absorption band at 835 cm^{-1}, which is assigned to =C—H out of plane bending of isoprene unit in the NR molecules [Fig. 10(B)]. The results are in
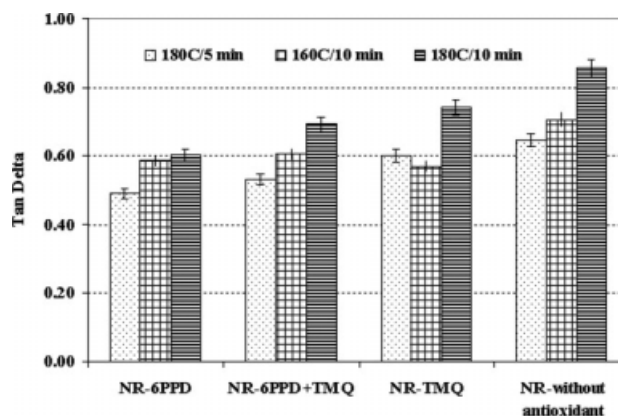

Figure 9 Tan δ at a frequency of 0.63 rad/s of NR without and with 4 phr of antioxidants at various mixing conditions.
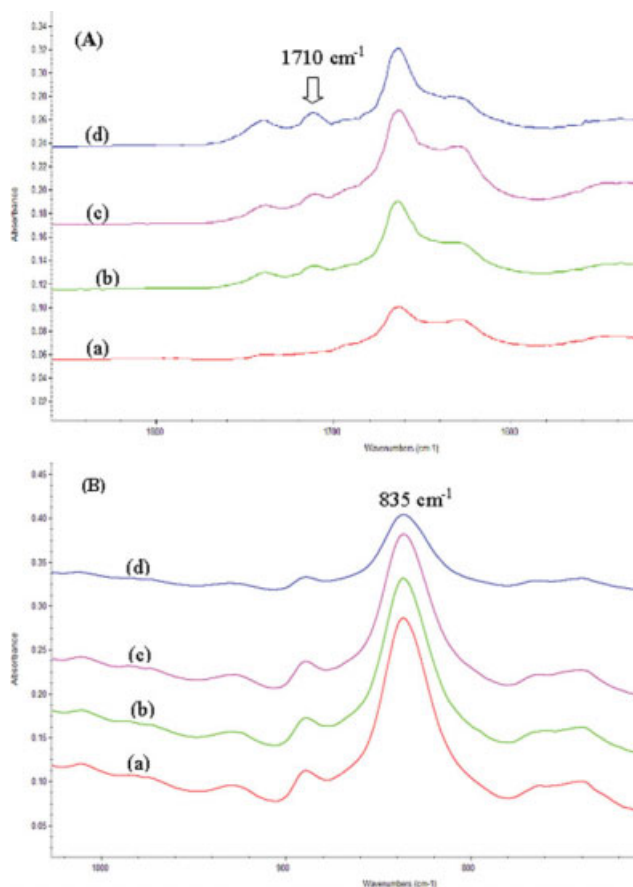
Figure 10 Infrared spectra upon thermo-oxidation of NR without antioxidant at different conditions, in a range of 1400–1900 cm^{-1} (A) and 730–980 (B), (a) unmasticated NR, (b) mixed at 180°C, 5 min, (c) mixed at 160°C, 10 min, and (d) mixed at 180°C, 10 min [carbonyl C=O stretching vibration at 1710 cm^{-1} and =C—H out of plane bending band at 835 cm^{-1}]. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

agreement with the previous reports.[4,7,8,10] The absorbance ratio of the carbonyl C=O stretching vibration at 1710 cm^{-1} to the =C—H out of plane bending vibration at 835 cm^{-1} could be used to estimate degree of oxidative degradation of NR molecules, as shown in Figure 11. It can be seen that the absorbance ratio of 1710/835 cm^{-1} increased with increasing mixing times and temperatures. Different types of antioxidants also depicted different absorbance ratios or carbonyl index. It is clear that the absorbance ratio of the NR mixed with 6PPD is lower than those of NR mixed with mixture of 6PPD and TMQ, NR mixed with TMQ and NR without antioxidant, respectively. Therefore, the effectiveness of antioxidants on protection of oxidative degradation of NR can be ordered based on their effectiveness as follows: 6PPD > 6PPD mixed with TMQ > TMQ. This is the same relationship as obtained by the moving die processability test.
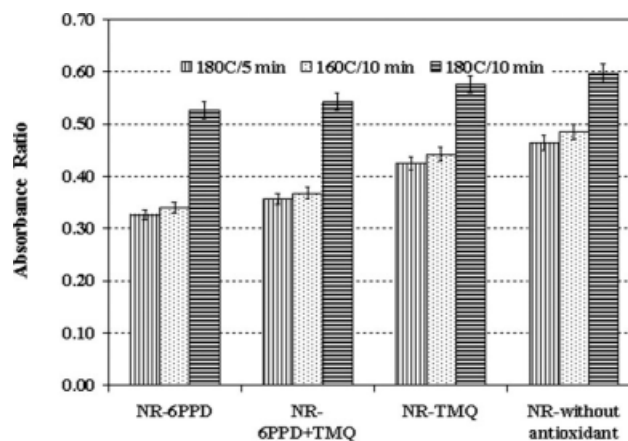
Figure 11 Absorbance ratio of the carbonyl C=O stretching band at 1710 cm^{-1} to the =C—H out of plane bending band at 835 cm^{-1} upon thermo-oxidation of NR without and with 4 phr of antioxidants.

Relationship between evolution of tan δ and IR absorption spectra

Figure 12 shows the relationship between tan δ and absorbance ratio of IR spectra at wave numbers of 1710 to 835 cm^{-1}. It is seen that tan δ values increased with increasing mixing time and temperature. This corresponds well with the increasing of carbonyl index based on the absorbance ratio. Longer mixing time at higher mixing temperature caused greater NR oxidative degradation as determined by increasing carbonyl index and tan δ values. This proved that the FTIR spectroscopy and moving die processability test are sensitive to the changes in molecular level of the NR molecules upon oxidative degradation. Thus, they can be used
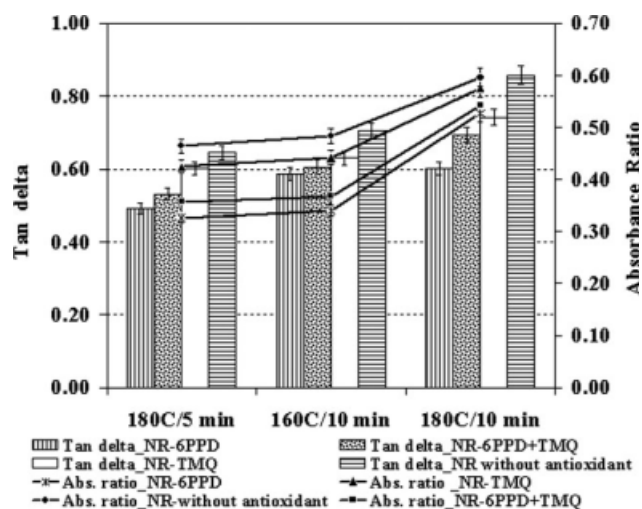

Figure 12 Comparison of tan δ at a frequency of 0.63 rad/s and absorbance ratio of 1710/835 cm^{-1} upon thermo-oxidation of NR without and with 4 phr of antioxidants.
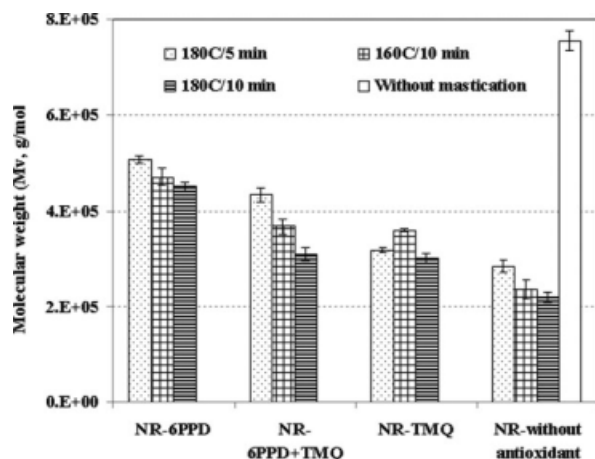
Figure 13 Viscosity average molecular weight (M_v) of NR without and with 4 phr of antioxidants at different mixing conditions.

to evaluate the oxidative degradation of the natural rubber molecules.

Viscosity average molecular weight

Viscosity average molecular weight ($\bar{M}_v$) was determined to identify a change in molecular weight of NR due to oxidative degradation. The results are shown in Figure 13. These are used to clarify and confirm the trend of tan δ and carbonyl index. It is seen that the molecular weight decreased with increasing mixing times and temperatures. In addition, the addition of 6PPD in NR resulted in the highest values of viscosity average molecular weight of NR, followed by the mixture of 6PPD with TMQ, TMQ, and NR without antioxidant, respectively. Therefore, a prolonged mixing and an increase in mixing temperature lead to greater oxidative degradation, as indicated by decreasing of viscosity average molecular weight. Moreover, incorporation of antioxidant into NR caused an improvement in antioxidative degradation as indicated by higher value of viscosity average molecular weight.

CONCLUSIONS

Oxidative degradation of NR was estimated and identified by the changes of molecular structure as indicated by the increase in tan δ and the chemical changes detected by FTIR spectroscopy. This provides preliminary assessment of the oxidative degradation of NR molecules by moving die processability test in combination with FTIR technique. The methods are useable to investigate or to compare various types and amount of antioxidants used in rubbers within a short testing time. Based on our observation, 6PPD provides better protection against oxidative degradation of NR under high heat and shearing action than TMQ. The antioxidants capability to protect NR from oxidative degradation can be ordered as: 6PPD > 6PPD mixed with TMQ > TMQ.

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