Journal of Metals, Materials and Minerals. Vol. 12 No. 1 pp. 51-57, 2002.

Effects of Particle Size and Amount of Carbon Black and Calcium Carbonate on Curing Characteristics and Dynamic Mechanical Properties of Natural Rubber

Saowaroj CHUAYJULJIT[1], Aopeau IMVITTAYA[1], Nuchanat NA-RANONG[2] and Pranut POTIYARAJ[1]

[1]Department of Materials Science, Faculty of Science, Chulalongkorn University
[2]Rubber Research Institute, Ministry of Agriculture and Cooperation

Abstract

This research extensively investigated the effects of particle size and amount of two types of fillers, namely, carbon black and calcium carbonate, on the curing characteristics and dynamic mechanical properties of vulcanized natural rubber. The experimental results indicated that, as the particle size of the carbon black decreased, the Mooney viscosity was increased effectively and the cure and scorch times were shortened. The same effect was obtained when the amount of fillers was increased. It could be assumed that the addition of carbon black decreased tan δ_{max}. The storage modulus (E') was affected by the particle size and the amount of carbon black added. With a small amount of carbon black added, E' was less than that of unfilled rubber. E' increased steadily as the amount of carbon black increased. At a particular amount of carbon black, E' of filled products was equal or larger than E' of unfilled rubber. The tensile modulus at 100% and 300% elongation was increased when tan δ_{max} was decreased. Such relationship could not be established in the case of products filled with calcium carbonate. The particle size and amount of calcium carbonate also had little effects on tan δ_{max} and storage modulus. The glass transition temperature was found to be affected insignificantly.

Keywords: Natural Rubber, Carbon Black, Calcium Carbonate, Dynamic Mechanical Properties

Introduction

Natural rubber is one of the most important agricultural products in Thailand which is currently the world largest natural rubber producer, with the production capacity of 1.8 million tons per year (Rubber Research Institute, 1999). As an elastomer, natural rubber is widely used in various applications, due to the fact that elastomers possess unique a properties, such as their ability to undergo a large elastic deformation and to absorb energy. Natural rubber products have been used in commodity applications, such as shoes, tires, rubber bands, tubes, etc. Recently, the applications of natural rubber have been expanded into engineering purposes, for example, machine parts, construction parts, automotive parts. For engineering applications, not only mechanical properties, but also dynamic mechanical properties at a sensible range of temperature, must be taken into account. It is of necessary to provide adequate data for engineers in designing rubber products with the required performance at all service temperatures.

Natural rubber has unique dynamic mechanical properties. The storage modulus (E') decreases with an increase in temperature upto about -10^{o}C. Below this temperature, the elastomer is in an enthalpy-dominant deformation regime. In this regime, the internal friction among the polymer chains during the deformation of the elastomer network structure is the controlling mechanism. (Trexler and Lee, 1985) Consequently, a high damping characteristic of the elastomers is expected. Above -10^{o}C, the storage modulus increases with an increase in temperature. This defines the entropy-dominant deformation regime (Trexler, *et al.* 1985; and Flory, 1953) in which the conformational change of polymer chains during the deformation of an elastomer network structure is the controlling mechanism. In other words, the elastomer network approaches a perfect network deformation and the elastomers exhibit low damping characteristics (Flory, 1953).

Practically, reinforcing fillers, along with other essential chemicals, are incorporated into natural rubber prior to the vulcanization process. Several investigations on relationships between the mechanical performance of natural rubber and the particle size and amount of fillers have been reported. (Trexler, *et al.* 1985; Potiyaraj, *et al.* 2001; Chuayjuljit, *et al.* 2001; and Wang, 1998). Carbon black is generally used as a reinforcing filler. It was found that as the particle size of carbon black is decreased, the mechanical properties of the rubber product are proportionally improved. The extent of the reinforcing effect is also increased when a larger amount of carbon black is incorporated. (Ghosh, *et al*. 1997; and Ghosh, *et al*. 2000)

For economic reasons, inert fillers, such as calcium carbonate, are also added in order to reduce the production cost by increasing the volume and mass of the products. In general, these inert fillers have little effects on mechanical properties and dynamic mechanical properties of the rubber products. However, the appropriate amount of inert fillers in the rubber compound must be taken into account in order to obtain the required performance. (Trexler and Lee, 1985)

Trexler reported that the state of cure had little effect on the glass transition temperatures and the storage moduli of the elastomers investigated. (Trexler and Lee, 1985) It was also pointed out that an elastomer having a desirable storage modulus with a low sensitivity to temperature changes can be developed by using a filler with a small particle size.

This research examines the effects of particle size and the amount of carbon black and calcium carbonate on curing characteristics, i.e. the Mooney viscosity, scorch time and cure time. The investigation also encompasses two dynamic mechanical properties, namely, the tan δ_{max} and the storage modulus. In addition, the relationship between tan δ_{max} and elastic modulus of natural rubber products would be proposed.

Materials and Methods

Rubber, carbon black, calcium carbonate, paraffinic oil, ZnO (zinc oxide), stearic acid, TMQ (2,2,4-trimethylbutyl-1,2-dihydroquinoline) and 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene-diamine) were incorporated in a kneader type KD.3 of Kneader Machinery Co.,Ltd.. Then the mixtures were made into rubber compounds by mixing with CBS (N-cyclohexyl-2-benzothiazyl sulphenamide), TMTD (tetramethylthiuram disulphide) and sulphur using a two-roll mill (Kodaira Seisakusho Model R11-3FF). The amounts of chemicals used in each compound are shown in **Table 1**. The raw compounds were then left overnight prior to the tests for the curing characteristics. The Mooney viscosity was determined according to ISO 289-1:1994(E) using a Mooney viscometer Model 123103 (Tech Pro, Inc.). A monsanto oscillating disk rheometer was used to determine the scorch time and cure time based on ISO 3417:1991(E).

Each compound was vulcanized in a vulcanized press (Chaicharoenkarnchang Co.,Ltd.) with a predetermined temperature and time as revealed by the rheometer. Two dynamic mechanical properties, i.e. the storage modulus (E') and the tan δ, were measured with a Perkin Elmer DMA7e in a tension mode. The frequency used in this experiment was 1Hz with a temperature range a -100^{o}C to 50^{o}C at a 5^{o}C/min heating rate.

In order to determine the elastic tensile modulus, the vulcanizates were cut into appropriate specimens. Then, the modulus was determined at 100% and 300% elongation according to ISO 37:1994(E) with an Instron Universal Testing Machine equipped with 500N loadcell at a static crosshead speed of 500 mm/min.

Table 1 Rubber Compounds.

Chemicals	Amount in the Compound (part per hundred rubber, phr)														Supplier
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
Natural Rubber STR 5L	100	100	100	100	100	100	100	100	100	100	100	100	100	100	Rayong Bangkok Rubber Co.,Ltd.
Filler															
Carbon Black N330[1]		30	45	60											Thai Carbon Black Co.,Ltd.
Carbon Black N550[1]					30	45	60								Thai Carbon Black Co.,Ltd.
Carbon Black N660[1]								30	45	60					Thai Carbon Black Co.,Ltd.
Calcium Carbonate[2]											15	30	45	60	FK Co.,Ltd.
Plasticizer Paraffinic Oil		6.7	10	13.3	6.7	10	13.3	6.7	10	13.3	3.3	6.7	10	13.3	Gurny Mooning Petrochemical Co.,Ltd.
Activator ZnO (white seal)	10	10	10	10	10	10	10	10	10	10	10	10	10	10	Univertures Public Co.,Ltd.
Stearic Acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2	Imperial Co.,Ltd.
Antidegradation TMQ	2	2	2	2	2	2	2	2	2	2	2	2	2	2	Flexsys Co.,Ltd.
6PPD	2	2	2	2	2	2	2	2	2	2	2	2	2	2	Flexsys Co.,Ltd.
Accelerator CBS	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	Flexsys Co.,Ltd.
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	Flexsys Co.,Ltd.
Vulcanizing Agent Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	Loxley Public co.,Tld.

[1]Particle sizes of N330, N550 and N660 are 26-30 nm, 40-48 nm and 49-60 nm, respectively.

[2]Light precipitated $CaCO_3$ with particle size of 390nm

Results and Discussion

Effects of Particle Size and Amount of Fillers on Curing Characteristics

The choice and loading of the filler affect the Mooney viscosity, flow behavior, scorch time and cure rate. (Robert, 1988) In general, the higher the volume loading, the higher the Mooney viscosity (Morton, 1973). Scorch time and cure time are also shorter when higher loading is employed. This is the case as shown in **Figure 1**. The incorporation of carbon black increased the Mooney viscosity of rubber. The viscosity was increased with respect to the amount of carbon black. As the particle size of the filler decreased, the viscosity was increased. On the other hand, the viscosity of the calcium carbonate filled rubber was changed slightly. This is due to the effect of bound rubber. During the milling process, part of the rubber becomes attached to fillers so that it cannot be extracted with regular rubber solvents. This insoluble rubber is called the bound rubber. Fine fillers bind high percentages of rubber, while coarse fillers bind practically none. Theoretically, reinforcing fillers affect the rubber viscosity according to the Einstein, Guth and Gold Equation (Morton, 1973) that is:

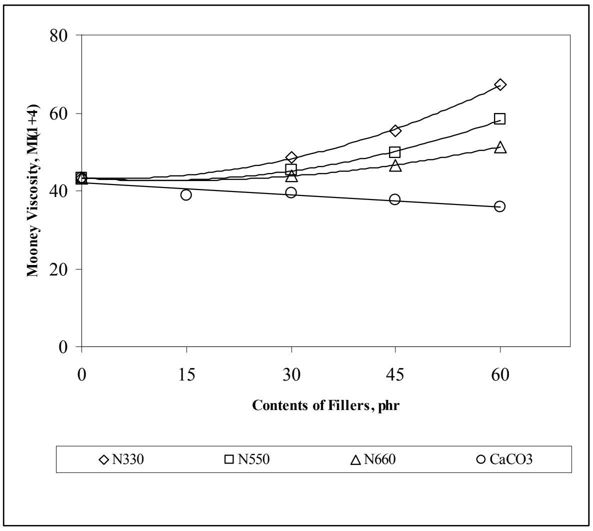

Figure 1 Mooney viscosity against the particle size & amount of fillers.

$$n_f = n_u \times (1 + 2.5C + 14.1C^2) \qquad (1)$$

where n_f and n_u are the viscosities of filled and unfilled rubber, C is the volume fraction of filler. Bound rubber is added to the filler fraction so that the viscosity of filled rubber increases accordingly. In the case of calcium carbonate, the surface area is very small and the bonding between calcium carbonate and rubber is negligible (Barlow, 1993); consequently the effect of the bound rubber is not obviously manifested as in the case of carbon black.

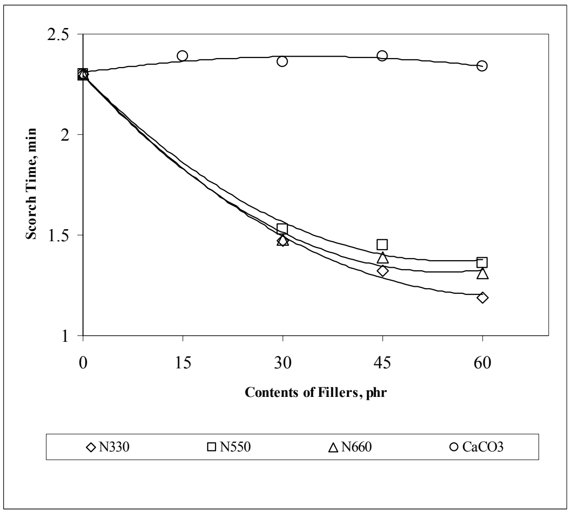

Figure 2 Scorch time against the particle size & amount of fillers

Figure 2 shows the scorch time with respect to the particle size and amount of fillers. Carbon black obviously reduced the scorch time, especially when the amount of carbon black increased. However, the particle size of carbon black had little effect on the scorch time. The effects of calcium carbonate were also insignificant. The effects of particle size and amount of fillers on the cure time, shown in **Figure 3**, were similar to those on the scorch time.

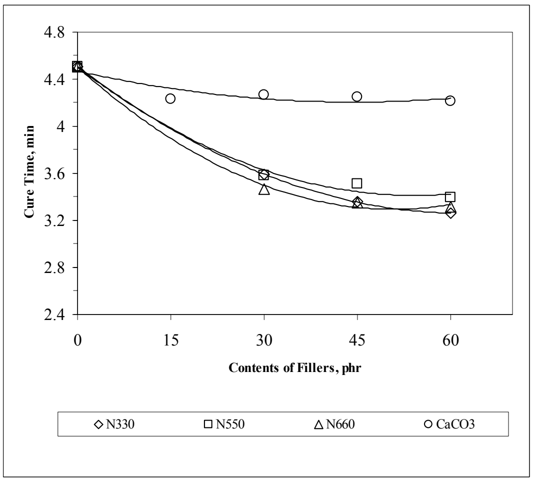

Figure 3 Scorch time against the particle size & amount of fillers.

The high surface area of carbon black generates more heat buildup in the compounds under shear conditions in the kneader. When a higher amount of fillers is used, heat is also generated in the system since the compound tends to be more viscous. As a consequence, the vulcanization reaction can occur more readily so that the Mooney viscosity increases while the scorch time and cure time are shortened. As calcium carbonate possesses a much larger particle size and a much lesser binding force with rubber, its lower surface area has little effect on the curing characteristics. (Roberts, 1988)

Effects of Particle Size and Amount of Carbon Black on Dynamic Mechanical Properties

The relationship of tan δ_{max} against the particle size and amount of fillers is shown in **Figure 4**. It was found that the addition of carbon black decreased tan δ_{max}, especially in the case of N330 which is the finest carbon black used in this experiment. As the particle size is finer, the surface area is higher, thus increasing the interaction between the molecules of rubber and carbon black. As a result, the chain flexibility is reduced and less mechanical energy could be transfer to the rubber molecules so that tan δ_{max} decreases. In the case of calcium carbonate which possesses a much smaller surface area than that of carbon black, the chain flexibility could occur easily thus increasing tan δ_{max}.

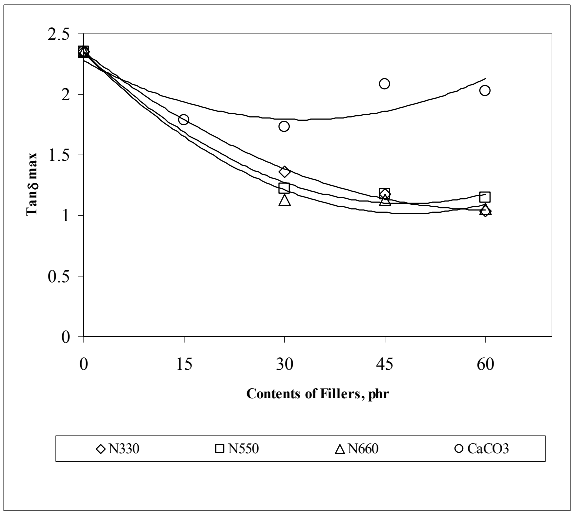

Figure 4 Tan δ_{max} against the particle size and amount of fillers.

The storage moduli were affected by the particle size and amount of carbon black added as shown in **Figures 5 – 8**. With the small amount of carbon black added, E' value is less than that of the unfilled rubber. This may be attributed to the minor effects of chain scission during processing, which is accentuated due to the increased viscosity of the carbon black-containing mix. The effect is emphasized in the case of rubber with finer carbon black since its viscosity is higher than that with the coarser one as discussed earlier. During the mixing process, the occluded rubber is formed. This is the rubber that finds itself in the internal void space of the structure aggregates. It is partially shielded from deformation when the rubber is strained. (Mark, *et al.* 1994) As the amount of carbon black increases the occluded rubber increases. This eventually overcomes the chain scission effect. The E' value, thus, increased steadily as the amount of carbon black was increased. Similarly, calcium carbonate also slightly increased the storage moduli when the amount was increased.

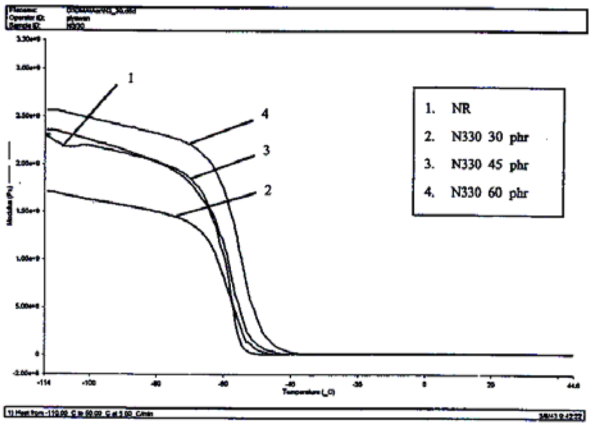

Figure 5 E' against temperature of rubber with 0, 30, 45 and 60 phr of N330 carbon black.

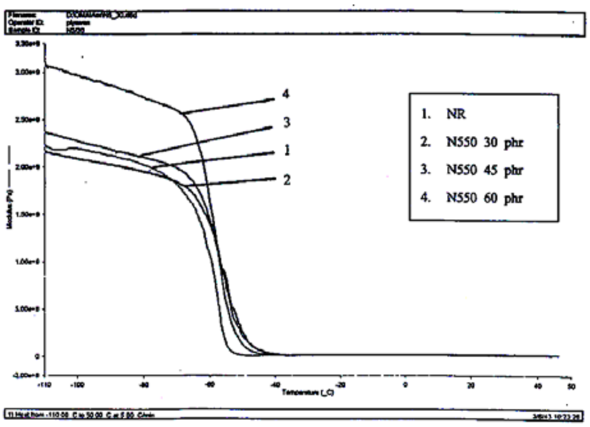

Figure 6 E' against temperature of rubber with 0, 30, 45 and 60 phr of N550 carbon black.

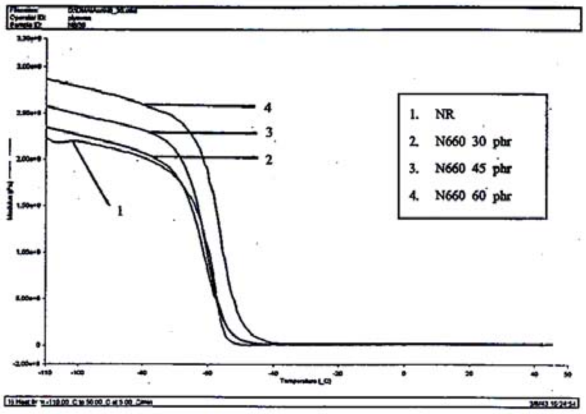

Figure 7 E' against temperature of rubber with 0, 30, 45 and 60 phr of N660 carbon black.

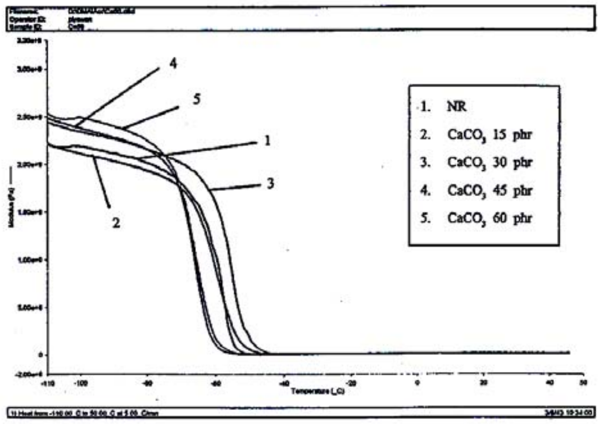

Figure 8 E' against temperature of rubber with 0, 15, 30, 45 and 60 phr of calcium carbonate.

Relationship between tan δ_{max} and Modulus

It can be seen in **Figure 9 and Figure 10** that the addition of carbon black increased the moduli at 100% and 300% elongation because the binding force between the carbon black and rubber molecules prohibited the movement of the polymer chain and reduced chain slippage.

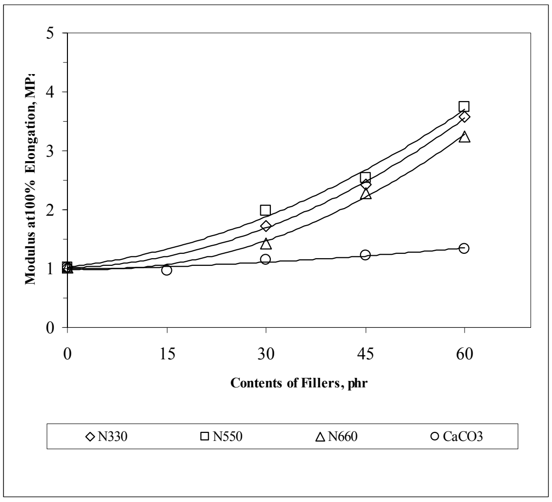

Figure 9 The modulus at 100% elongation against the particle size and amount of fillers.

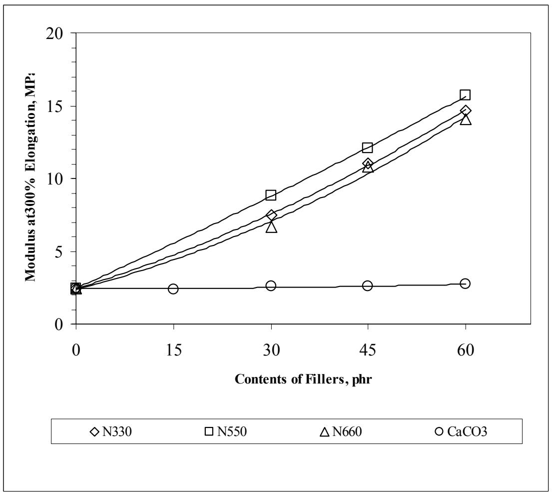

Figure 10 The modulus at 300% elongation against the particle size and amount of fillers.

The tensile force must be increased in order to obtain the same extent of elongation. As a consequence, the modulus was increased. From the experimental results, it was found that the relationships between particle size and modulus could not be assumed. Modulus of products was increased insignificantly when calcium carbonate was used. This is due to the fact that the bonding between filler and rubber is inferior since the $CaCO_3$ has much less surface area than carbon black.

The relationships between tan δ_{max} and modulus at 100% and 300% elongation are shown in **Figure 11 and Figure 12**. With respect to the amount of carbon black, it could be concluded that under tensile static force, the moduli at 100% and 300% were increased while tan δ_{max} results obtained from periodic force were decreased. In the case of $CaCO_3$, the relationship between tan δ_{max} and modulus could not be elaborated.

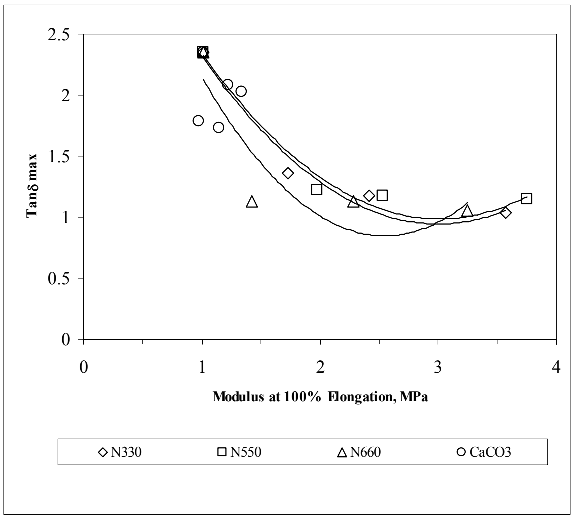

Figure 11 Relationship between Tan δ_{max} and Modulus at 100% elongation.

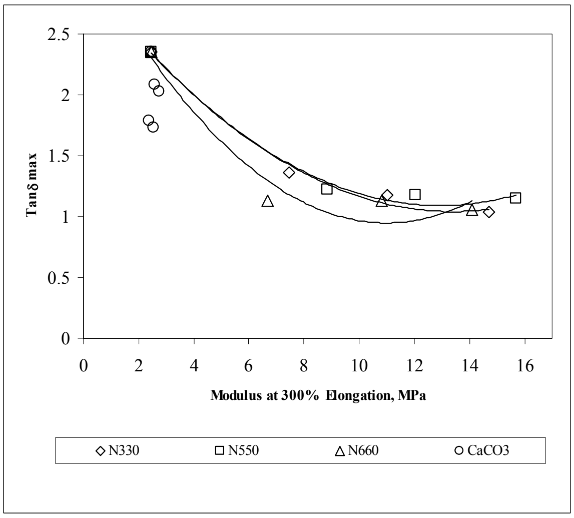

Figure 12 Relationship between Tan δ_{max} and Modulus at 300% elongation (correlation coefficient between –0.80 and –0.99)

Conclusions

Natural rubber is one of the most widely used elastomers for engineering purposes. The investigation of dynamic mechanical properties with a broad range of temperature would provide useful data in designing such materials. This research investigated the effects of particle size and amount of two important fillers, carbon black and calcium carbonate on curing characteristics and dynamic mechanical properties. It was found that the incorporation of carbon black resulted in shorter scorch and curing time so that time and energy could be saved. Calcium carbonate, although slightly affected the curing characteristics, may be used in order to reduce the production cost. This should be done with consideration since some mechanical properties may be worsened. The tan δ_{max} value was decreased as a larger amount of carbon black was incorporated into the rubber, especially when the particle size of carbon black is smaller. On the other hand, the tan δ_{max} value was increased with the addition of calcium carbonate. The storage modulus was also affected by particle size and amount of carbon black, as well as calcium carbonate. The relationship between tan δ_{max} and modulus was also developed. Under static tensile force, the moduli at 100% and 300% were increased while tan δ_{max} obtained from periodic tensile force was decreased. Such a relationship could not be established in the case of $CaCO_3$. Further study on relationships between mechanical and dynamic mechanical properties may lead to economical alternatives to current methods for dynamic mechanical property determination. These findings may be useful as a guideline for the development of rubber compounds for engineering purposes with required performance.

References

Barlow, F. W. 1993. *Rubber Compounding: Principles, Materials and Techniques.* 2nd ed. New York, Marcel Dekker.

Chuayjuljit, S., Eiumnoh, S. and Potiyaraj, P. 2001. Using Silica from Rice Husk as a Reinforcing Filler in Natural Rubber. *J. Sci. Res. Chula. Univ.* **26(2)** : 127-138.

Flory, P. J. 1953. *Principles of Polymer Chemistry*. New York, Cornell Univ. Press.

Ghosh, A. K., Maiti, S., Adhikari, B., Ray, G. S. and Mustafi, S. K. 1997. Effect of Modified Carbon Black on the Properties of Natural Rubber Vulcanizate. *J. Appl. Polym. Sci.* **66(4)** : 683-693.

Ghosh, P. and Chakrabati, A. 2000. Conducting Carbon Black Filled EPDM Vulcanizates: Assessment of Dependence of Physical and Mechanical Properties and Conducting Character on Variation of Filler Loading. *Eur. Polym. J.* **36(5)** : 1043-1054.

Mark, J. E., Erman, B. and Eirich, F. R. 1994. *Science and Technology of Rubber.* 2nd ed. New York, Academic Press.

Morton, M. 1973. *Introduction to Rubber Technology.* 2nd ed. New York, Reinhold Publishing.

Potiyaraj, P., Panchaipech P. and Chuayjuljit, S. 2001. Using Water Hyacinth Fiber as a Filler in Natural Rubber. *J. Sci. Res. Chula. Univ.* **26(1)** : 11-18.

Roberts, A. D. 1988. *Natural Rubber Science and Technology.* New York, Oxford University Press.

Rubber Research Institute. 1999. *Thailand Rubber Statistics* Bangkok, Ministry of Agriculture and Cooperation.

Trexler, H. E. and Lee, M. C. H. 1985. Effect of Types of Carbon Black and Cure Conditions on Dynamic Mechanical Properties of Elastomers. *The American Chemical Society, Rubber Division Meeting*, Research Publication GMR-4908 : 27 p.

Wang, M. J. 1998. Effect of Polymer-Filler and Filler-Filler Interactions on Dynamic Properties of Filled Valucanizates. *Rubber Chem. Technol.* **71(3)** : 520-589.

(Revised version accepted September 9, 2002)