Application of Lime Kiln Dust as a Filler in the Natural Rubber Industry

Wanvimon Arayapranee,[1] Garry L. Rempel[2]

[1]Department of Chemical and Material Engineering, Rangsit University, Phathum Thani 12000, Thailand
[2]Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

ABSTRACT: Lime kiln dust (LKD) obtained from kraft chemical recovery systems by conversion of calcium carbonate ($CaCO_3$) back into calcium oxide (CaO) for reuse in the causticizing process, is mainly composed of $CaCO_3$. A two-stage conventional mixing procedure was used to incorporate LKD into natural rubber (NR). For comparison purposes, four commercial fillers, stearic acid coated $CaCO_3$, ground $CaCO_3$, silica, and carbon black, were also used. The effect of these fillers on the curing characteristics and mechanical properties of NR materials at various loadings ranging from 0 to 60 phr were studied. The results indicate that the use of LKD filler resulted in a lower Mooney viscosity and shorter curing time in the NR materials. The incorporation of LKD into NR improved the Young's modulus and hardness but decreased the tensile strength and tear strength. However, LKD was better in processability than the commercial fillers. Scanning electron micrographs revealed that the morphology of the rubbers filled with reinforcing fillers, such as silica and carbon black, was finer and more homogeneous compared to the those of the rubbers filled with LKD and commercial $CaCO_3$. The dispersion of LKD and commercial $CaCO_3$ fillers in the rubber matrix was discontinuous, which in turn, generated a weak structure compared with the reinforcing fillers. According to these observations, LKD could be used as a cheaper filler for NR materials where improved mechanical properties are not critical. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 263–272, 2011

Key words: carbon black; compounding; fillers; rubber; silicas

INTRODUCTION

Natural rubber (NR) is notable for its versatility as an elastomeric material; its most important property is its ability to undergo large elastic deformations before returning to its original shape in a reversible way. Rubbers are rarely used in their unmodified form when it comes to applications. They must often be modified with fillers to improve their modulus and failure properties (tensile and tear strength) and reduce unit manufacturing costs while their high levels of product quality and performance are maintained. Many studies on the mechanical properties of various rubber compounds have been reported, including studies on the effect of the type and amount of rubber and filler and the interaction between rubbers and fillers. A variety of black and nonblack fillers of the reinforcing and nonreinforcing types cater to this need. Among several fillers, silica and carbon black are the most important reinforcing agents used in compounding recipes.[1–9] Despite being well known for their strong interactions with rubbers, these fillers are relatively expensive compared with natural fillers. The effects of fillers on the mechanical and other properties of the compounds depend strongly on their shape, size and size distribution of the primary particles and their aggregates, surface characteristics, and degree of dispersion and distribution.[10] One of the most important fillers used in large quantities in particulate-filled polymers is calcium carbonate ($CaCO_3$). Much work[11–14] has been done to study the use of $CaCO_3$ as a filler for polymeric materials. It not only lowers the cost but also improves the mechanical properties, including the modulus, hardness, toughness, dimensional stability, thermal resistance, and flame retardancy. However, the advantages offered by the use of fillers can be exploited only if the particles are distributed homogeneously in the polymer matrix. To improve the interfacial adhesion, the treatment of the filler with coupling agents or reactive surface modifiers is generally used.[15,16] Kiss et al.[17] investigated the effect of aggregation in polypropylene composites containing seven different precipitated $CaCO_3$ fillers coated with stearic acid. They observed that the coated fillers formed much looser aggregates with more diffuse interphases than the uncoated particles.

TABLE I
Ingredients Used in This Study

Ingredient	Amount (phr)[a]	Grade/supplier
NR	100	STR XL/Yala Latex Industry Co., Ltd., Yala, Thailand
ZnO	5.0	Commercial/Gradmann, Bangkok, Thailand
Stearic acid	2.0	Commercial/P. T. Cisadaneraya Chemical, Jakata, Indonesia
N-Cyclohexyl-2-benzothiazole-2-sulfenamide	1.8	Flexsys Co., Ltd., Frankfurt, Germany
Sulfur	2.4	Commercial/Chemmin Co., Ltd., Bangkok, Thailand
Filler: LKD (wasted $CaCO_3$)	Variable (0–60)	Advance Agro Public Co., Ltd., Prachinburi, Thailand
Stearic acid coated $CaCO_3$	Variable (0–60)	Surint Omya Chemicals (Thailand) Co., Ltd., Bangkok, Thailand
Commercial $CaCO_3$	Variable (0–60)	Quality Minerals Public Co., Ltd., Bangkok, Thailand
Silica (SiO_2)	Variable (0–60)	Hi-Sil 233s/PPG-Siam Silica Co., Ltd., Bangkok, Thailand
Carbon black	Variable (0–60)	N330/Thai Carbon Product Co., Ltd., Bangkok, Thailand
Poly(ethylene glycol) (PEG 3350)[b]	2.0	Brand Co., Ltd., Bangkok, Thailand

[a] phr = parts per hundred of rubber.
[b] Only in batches having silica as a filler.

Sahnoune et al.[18] observed that the incorporation of $CaCO_3$ into a fixed 75 : 25 wt % blend ratio of high-density polyethylene and polystyrene led to an increased stiffness of the blends, whereas the impact resistance showed a decrease. Supaphol et al.[19] studied the effects of $CaCO_3$ with various particle sizes (1.9, 2.8, and 10.5 μm), contents (0–40 wt %), and type of surface modification (uncoated, stearic acid coated, and paraffin-coated) on the mechanical properties of syndiotactic polypropylene/$CaCO_3$ compounds. They reported that the tensile strength was found to decrease and the Young's modulus increased with increasing $CaCO_3$ content. Both types of surface treatment on the $CaCO_3$ particles reduced the tensile strength and Young's modulus but improved the impact resistance.

Lime kiln dust (LKD) is a byproduct obtained from kraft chemical recovery systems to reclaim spent chemicals, which are then reused in the process. The function of the lime kiln is to convert $CaCO_3$ back into calcium oxide (CaO) for reuse in the causticizing process. Because of the nature of the reburning of lime mud ($CaCO_3$), a large amount of dust is generated. The dust has to be removed from the mud filter before the discharges are released to the environment. LKD consists mainly of $CaCO_3$ and has shown good potential as a filler in rubber. The application of fillers derived from LKD for use in rubber compounding has attracted interest because of its low cost and environmental friendliness. Today, fillers derived from industrial waste have become a focus of attention. However, no serious attempt has been made to evaluate the use of LKD as a reinforcing filler for NR. Because LKD is readily available at an extremely low cost as an unwanted byproduct from kraft lime kilns, the determination of useful applications for LKD will certainly help to alleviate problems related to the disposal of the waste.

The mechanical properties of filled rubbers are usually described in terms of tensile and tear strength, Young's modulus, and hardness. The mechanical properties of filled rubbers depend mainly on the type of filler, filler loading, filler dispersion, filler surface area, and interaction between the filler and the rubber matrix. In this study, LKD was incorporated into NR, and the effect of filler loading compared to commercial fillers, stearic acid coated $CaCO_3$, ground $CaCO_3$, silica, and carbon black was investigated by the examination of the processability and mechanical properties as performance indicators.

EXPERIMENTAL

Materials

Details of the mixing ingredients and rubber formulas used are shown in Table I. All of the mixing ingredients were used as received. The particle size distribution was measured with a particle size analyzer (Mastersizer-S, Malvern Instruments, Ltd., Worcestershire, England). The surface area of the fillers was determined by the Brunauer–Emmett–Teller method with an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). The physical properties of fillers are presented in Table II. The Fourier transform infrared (FTIR) spectra of LKD and ground $CaCO_3$ were obtained with a Tensor 27 series spectrometer (Bruker Optics Ettlingen, Germany). Figure 1 shows the FTIR spectra of the LKD and ground $CaCO_3$. They both had absorption peaks around 1430, 875, and 712 cm^{-1}. It is well known that $CaCO_3$ shows strong absorption peaks at 1430, 875, and 712 cm^{-1} in its IR spectrum. These peaks are attributable to the vibration of the carbon–oxygen double bonds in the carbonate ion. According to Figure 1, LKD showed similar results compared to ground $CaCO_3$; this suggested that LKD in this case was mainly composed of $CaCO_3$.

Preparation of the rubber compounds

A two-stage mixing procedure was used to prepare all of the compounds. In the first stage, the mixing

TABLE II
Physical Properties of the Fillers

Filler	Mean particle size (µm)	Surface area (m²/g)
LKD	7.5	5.24
Stearic acid coated $CaCO_3$	5	3.24
Commercial $CaCO_3$	5.3	2.8
Silica	18	165
Carbon black	20.2	84

was carried out in a dispersion kneader machine (Kneader Machinery Co., Ltd., Tainan Shiann, Taiwan) with a fill factor of 0.7 and at a chamber temperature of 75°C and a rotor speed of 40 rpm. NR was initially masticated in the mixer for 2 min before the stearic acid and zinc oxide (ZnO) were added. After 1 min of mixing, the filler was added, and the mixing process continued for a further 6 min. Finally, the N-cyclohexyl-2-benzothiazole-2-sulfenamide accelerator was added and mixed for 3 min. The mixture was then discharged, and sulfur was added for the second step and mixed with a two-roll mill (Kodaira Seisakusho Co., Ltd., Tokyo, Japan) with a friction ratio of 1 : 1.1 at 70°C for 3 min.

Cure characteristics

The cure characteristics were studied with a rheometer (TECH-PRO, Cuyahoga Falls, OH) according to ISO 3414 for 30 min at 150°C. The Mooney viscosity (ML_{1+4} at 100°C) was determined with a Mooney viscometer (TECH-PRO). The testing procedure was conducted according to the method described in ISO 289-1.

Vulcanization process

A conventional vulcanization system was used for curing. All compounds were compression-molded at 150°C with a force of 17.5 MPa with a hydraulic hot press (Power Drive System Co., Ltd., Bangkok, Thailand) according to their respective cure times (t_{90}'s), as determined with a TECH-PRO instrument.

Mechanical properties

The tensile properties were determined on an Instron testing machine (model 1011, Norwood, MA) with C-type dumbbell specimens according to ASTM D 412. The specimens, with a geometry of a dumbbell shape 2 mm in thickness, 25 mm in width, and 115 mm in gauge length, were cut into standard test pieces with a Wallace die cutter (Surrey, England). The crosshead speed was set at 500 mm/min. At least six specimens were tested for each vulcanizate. The average value and the standard deviation (SD) of the data points around the average value were then calculated and are reported for each case.

The tear strength is a measure of the resistance of a material to tear forces. One calculates the tear strength of a notched specimen by dividing the maximum load by the thickness of the specimen. The tear strength was measured in a Lloyd instrument (Düsseldrof, Germany) according to ASTM D 624 (die C) with unnicked 90° test pieces. The tear properties were tested at a speed of 500 mm/min. At least five specimens were tested for each vulcanizate. The average value and SD of the data points around the average value were then calculated and are reported for each case.

The hardness measurement of the samples was done according to ASTM D 2240 (Shore A) with a Lever loader (model 917, Mount Holly, NJ). At least five specimens were tested for each vulcanizate. The average value and SD of the data points around the average value were then calculated and are reported for each case.

Scanning electron microscopy (SEM)

SEM studies of the compounds' tensile fracture surfaces were carried out on gold-coated samples with a JEOL microscope (model JSM 5600 LV, Tokyo, Japan) at a magnification of 3000×. The different shapes of the fillers were also examined with a scanning electron microscope at 5000 and 10,000× magnification.
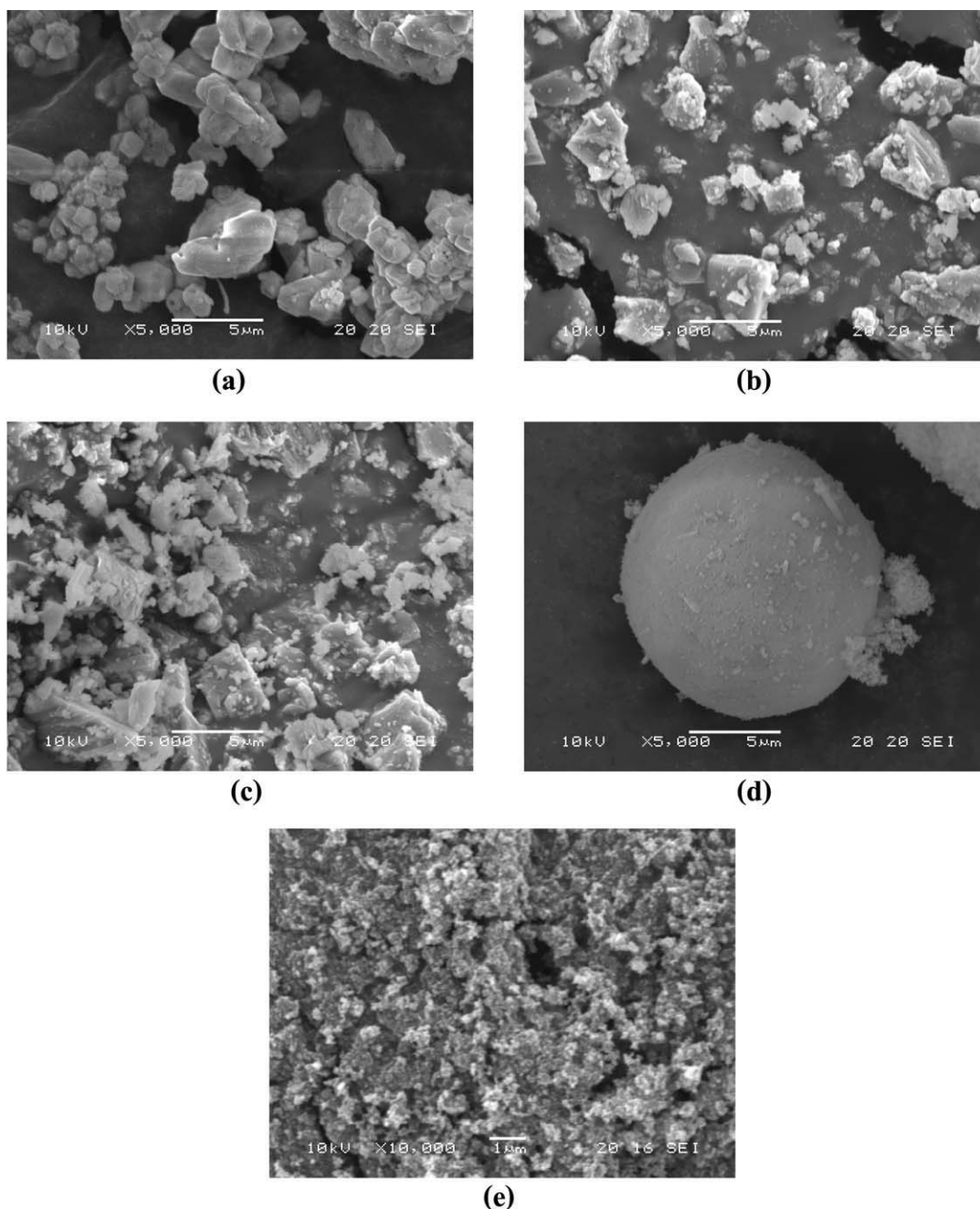
RESULTS AND DISCUSSION

SEM studies of the filler particles

SEM micrographs of the various shapes of the filler particles at different magnifications are shown in Figure 2. As shown, $CaCO_3$ had irregular, approximately cubical particles [Fig. 2(a–c)]. LKD had an aggregated
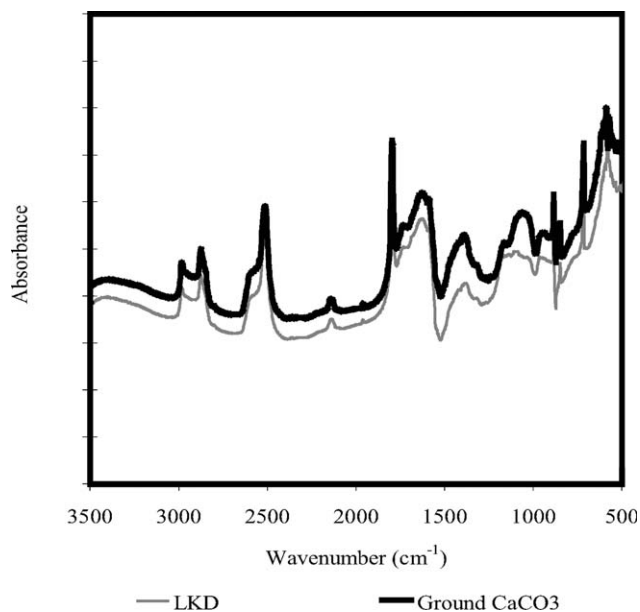


Figure 1 FTIR spectra of the LKD and ground $CaCO_3$.

Figure 2 SEM micrographs of the different fillers: (a) LKD at 5000× magnification, (b) stearic acid coated CaCO₃ at 5000× magnification, (c) ground CaCO₃ at 5000× magnification, (d) silica at 5000× magnification, and (e) carbon black at 10,000× magnification.

structure [Fig. 2(a)], wherein the aggregates existed in clusters. Figure 2(c) shows the formation of fewer aggregates in ground CaCO₃ compared to LKD. Minimal aggregation was observed in the morphology of the coated CaCO₃ because the coating of CaCO₃ with stearic acid led to a decrease in the surface tension; this resulted in decreased aggregate formation [Fig. 2(b)]. The particle shape of the silica, shown in Figure 2(d), was spherical except for a very few irregularly shaped impurities. Apparently, unlike silica, the carbon black morphology contained spheroidal units, which tended to be joined together in chains or clusters [Fig. 2(e)]. Beaucage et al.,[20] in their studies, suggested that the carbon black aggregates had smooth surfaces. Meanwhile, according to Figure 2(a–c), the CaCO₃ aggregates showed angular surfaces.

Cure characteristics and processability of the NR compounds

Various fillers were incorporated with loadings ranging from 0 to 60 phr (parts per hundred of rubber) at
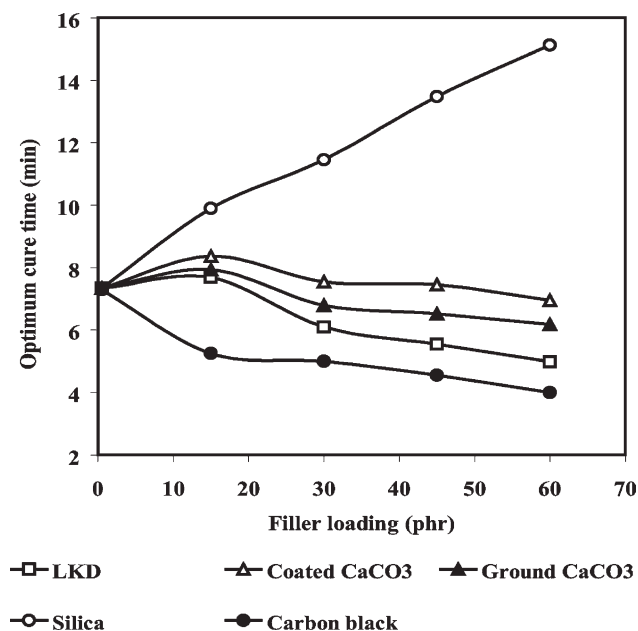
Figure 3 Relationship between the filler loading and optimum t_{90} (ML$_{1+4}$ at 100°C) of the NR compounds filled with various fillers.

15-phr intervals in the NR compounds to study the effect of the filler loading on the cure properties of the NR compounds, as shown in Figure 3. The compounds were vulcanized for their optimum t_{90}. For the optimum t_{90}, compared to the unfilled compound, an increase in the loading of CaCO$_3$ and carbon black decreased the optimum t_{90}. However, at a similar filler loading, the carbon-black-filled NR compounds exhibited the shortest t_{90} followed by NR compounds filled with LKD, ground CaCO$_3$, coated CaCO$_3$, and silica. For carbon black, the reduction of t_{90} was due to the role of carbon black, which accelerated the vulcanization process. With silica, there was a different trend in the cure characteristics. The filler properties that have the greatest influence on rubber processing and vulcanizes are the particle size, surface area and character, and structure. LKD had a large particle size, irregularly shaped particles (nonspherical particles with angular shapes), and an aggregated structure. At any particular loading, t_{90} of the LKD-filled NR was less than those of the NRs filled with ground and coated CaCO$_3$. The aggregated structure of the LKD filler [Fig. 2(a)], which implied a poor filler–rubber interaction, might have been responsible for the catalytic effect of this filler on NR vulcanization. The optimum t_{90} tended to increase with increasing silica content. The retardation effect found in the silica vulcanizate was attributed to a silica–accelerator system interaction. This filler reacted with ZnO and, subsequently, reduced the zinc available; this slowed the vulcanization process. Other researchers[11] observed a similar trend in other CaCO$_3$-filled NR compounds.

The effect of the filler loading on the Mooney viscosity of the compounds is shown in Figure 4. For NRs filled with silica and carbon black, the Mooney viscosity increased significantly with an increase in the filler loading. However, for CaCO$_3$ fillers, the change of this property with filler loading was only small. The silica-filled NR materials had the highest Mooney viscosity followed by those filled with carbon black, coated CaCO$_3$, ground CaCO$_3$, and LKD. In the mixing state, a low surface area (Table II) and interaction between the fillers and rubbers gave rise to a lower viscosity, as compared to rubbers filled with reinforcing fillers. The presence of reinforcing fillers in the rubber matrix reduced the mobility of the rubber's macromolecular chains. The high values of viscosity for silica- and carbon-black-filled NR materials indicated that there was a high restriction to the molecular motion of the macromolecules, which was probably caused by the greater interaction between both fillers and the rubber matrix. The lowest Mooney viscosity in the LKD-filled NR indicated that it could be processed more easily than NRs containing other fillers.
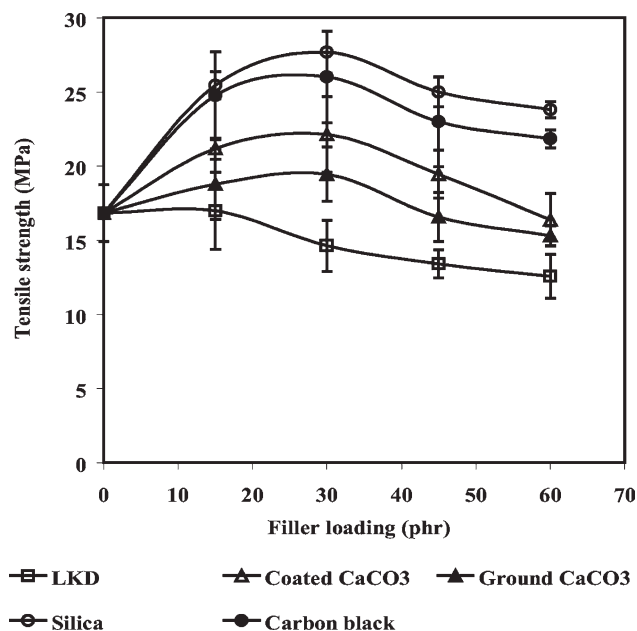
Mechanical properties of the NR compounds

Tensile properties

Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most applications. Various fillers were incorporated at different ratios up to 60 phr in the NR compounds to study the effect of the filler
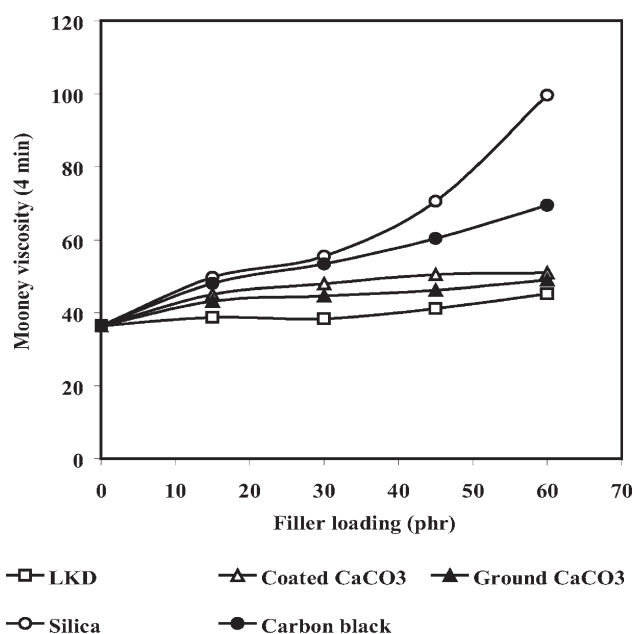
Figure 4 Relationship between the filler loading and Mooney viscosity of the NR compounds filled with various fillers.
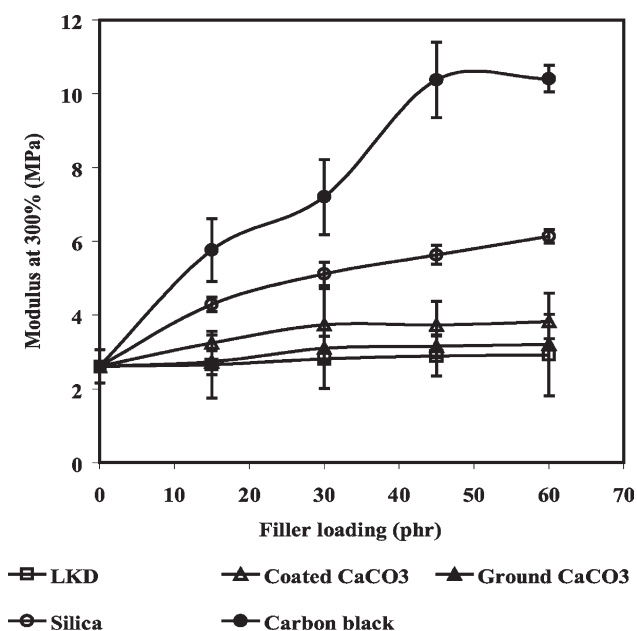
Figure 5 Effect of the filler loading on the tensile strength of the LKD, stearic acid coated $CaCO_3$, ground $CaCO_3$, silica, and carbon-black-filled NR compounds.

loading on the mechanical properties of the filled NR compounds. Figure 5 shows the tensile strength of the NR compounds as a function of the filler loading. The effects of filler loading on the tensile strength of the NR compounds increased or decreased with the incorporation of filler. At a similar filler loading, the silica-filled NR compounds gave the highest tensile strength, followed by those filled with carbon black, coated $CaCO_3$, ground $CaCO_3$, and then, LKD. The tensile strength of the NR compounds containing reinforcing fillers increased with filler loading until a maximum level was reached ($\sim$ 30 phr), and then, the property started to decrease with increasing filler loading. The detrimental effect on the tensile strength at high filler loadings may have been due to a dilution effect or to the aggregation of the filler. Rigbi[21] reported that the reinforcing filler increases the tensile strength up to a maximum filler loading of the elastomer, after which a detrimental effect on the tensile strength at high loadings may be attributed to the dilution effect or aggregation of the filler. On the other hand, a negative effect on the tensile strength was observed for the LKD-filled NR compounds. The tensile strength of the filled NR compounds decreased with increasing LKD loading because of the inability of the filler to support stresses transferred from the rubber matrix. Even with reinforcing filler with a larger particle size than $CaCO_3$, the tensile strength of the NR compounds containing a reinforcing filler was higher than that of the $CaCO_3$-filled NR compounds. We believe that a larger surface area (Table II) and uniform dispersion of both

silica and carbon black in the rubber compounds contributed to better tensile strength. In addition, for angular-shaped fillers such as $CaCO_3$ [Fig. 2(a–c)], their capability to support stresses transmitted from the rubber matrix was rather poor. Thus, the strength enhancement in the $CaCO_3$-filled compounds was, in general, much lower than that of NR compounds containing a reinforcing filler. We observed that the tensile strength of LKD was lower compared to those of the coated and ground $CaCO_3$ compounds. On the basis of a morphology study (shown in Fig. 2), we found that the aggregation of LKD resulted in inhomogeneous distribution, which weakened the interaction between the filler and the matrix and, thus, led to undesirable material properties. Supaphol et al.[19] observed a similar trend in strength from their study of $CaCO_3$-filled syndiotactic polypropylene compounds.

Figure 6 shows the effect of the filler loading on the modulus at 300% elongation of the rubber blends; this was an indication of the material stiffness for NR compounds containing fillers. Fillers are known to increase the modulus, provided that the modulus of the filler is higher than that of the polymer matrix. The modulus of the filled compounds increased with increasing filler loading. Carbon black and silica improved the stiffness of the rubber blends, whereas $CaCO_3$ materials showed a small increase in this property. The most important contribution to the elastic modulus arose from polymer–filler interactions; these can be increased when a good dispersion of the filler is characteristic of the particles and is also dependent on the chemical

Figure 6 Effect of the filler loading on the modulus values at 300% LKD, stearic acid coated $CaCO_3$, ground $CaCO_3$, silica, and carbon-black-filled NR compounds.
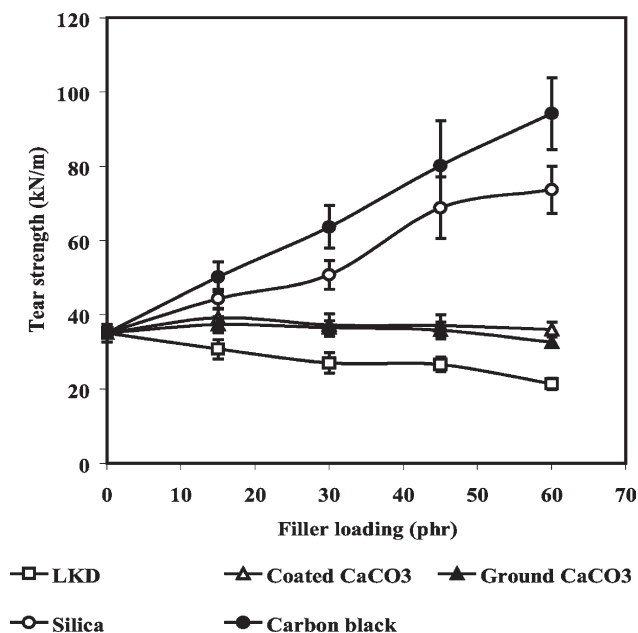
Figure 7 Effect of the filler loading on the tear strength of the LKD, stearic acid coated CaCO₃, ground CaCO₃, silica, and carbon-black-filled NR compounds.

nature of the polymer. As more filler particles were introduced into the rubber, the elasticity of the rubber chains decreased, which resulted in higher stiffness properties. At a similar filler loadings, the carbon-black-filled NR compounds gave the highest modulus at 300% elongation, followed by NR compounds filled with silica, coated CaCO₃, ground CaCO₃, and then, LKD. Sae-Oui et al.[9] also reported that surface area is the most important factor controlling the tensile strength, whereas the surface activity controls the modulus. As shown in Figure 6, LKD-filled NR compounds showed a comparable modulus with NR compounds filled with ground CaCO₃; however, a slightly lower modulus was observed in comparison with that of the compounds filled with coated CaCO₃. The aggregation of LKD caused the dispersion of the filler into the rubber to become inhomogeneous, and this likely weakened the modulus of the LKD-filled NR compounds. Luyt et al.[22] reported that the distribution of filler particles in a polymer–matrix greatly influences the modulus of the composites.

Tear strength

Figure 7 shows the tear strength of the filled rubber materials. The tear strength, like the tensile strength, was affected by the surface area. At a similar filler loadings, the carbon-black-filled NR compounds gave the highest tear strength, followed by the NRs filled with silica, coated CaCO₃, ground CaCO₃, and then, LKD. As shown, the addition of silica or carbon black considerably increased the tear strength of

the rubber materials. This was mainly attributed to the reduction of stress concentration at the crack tips in the presence of the filler, particularly for the highly smooth surface particles. In contrast, the addition of the CaCO₃ substance fillers slightly reduced the tear strength of the rubber materials. This may have been due not only to their low rubber–filler interaction but also to their angular particle shape. For this reason, both the tensile and tear strengths were decreased with increased loading of the CaCO₃-based fillers, with LKD showing the greatest decrease in tear strength.

Hardness

Figure 8 shows the effect of the filler loading on the hardness of the rubber materials, which exhibited similar trends; the hardness of the filled rubber materials increased with filler loading. This was simply due to the fact that the incorporation of more rigid filler particles into rubber reduced the elasticity of the rubber chains and led to more rigid rubber materials. As expected, CaCO₃-filled rubber materials had a lower modulus and hardness than the corresponding rubber materials with carbon black and silica. At a similar filler loading, carbon-black-filled NR compounds gave the highest hardness, followed by the NR compounds filled with silica, coated CaCO₃, ground CaCO₃, and then, LKD. The cubical particle with an angular shape might have influenced the bonding at the interface and, thus, lowered the hardness. The effect of the filler loading on
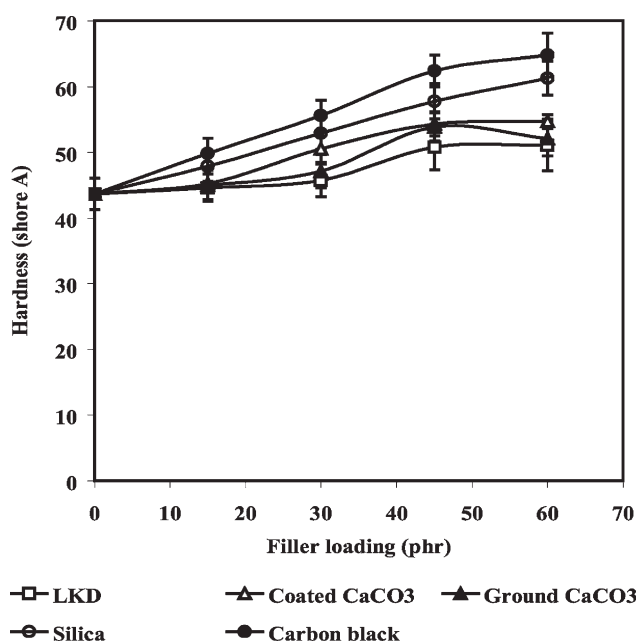
Figure 8 Effect of the filler loading on the hardness of LKD, stearic acid coated CaCO₃, ground CaCO₃, silica, and carbon-black-filled NR compounds.
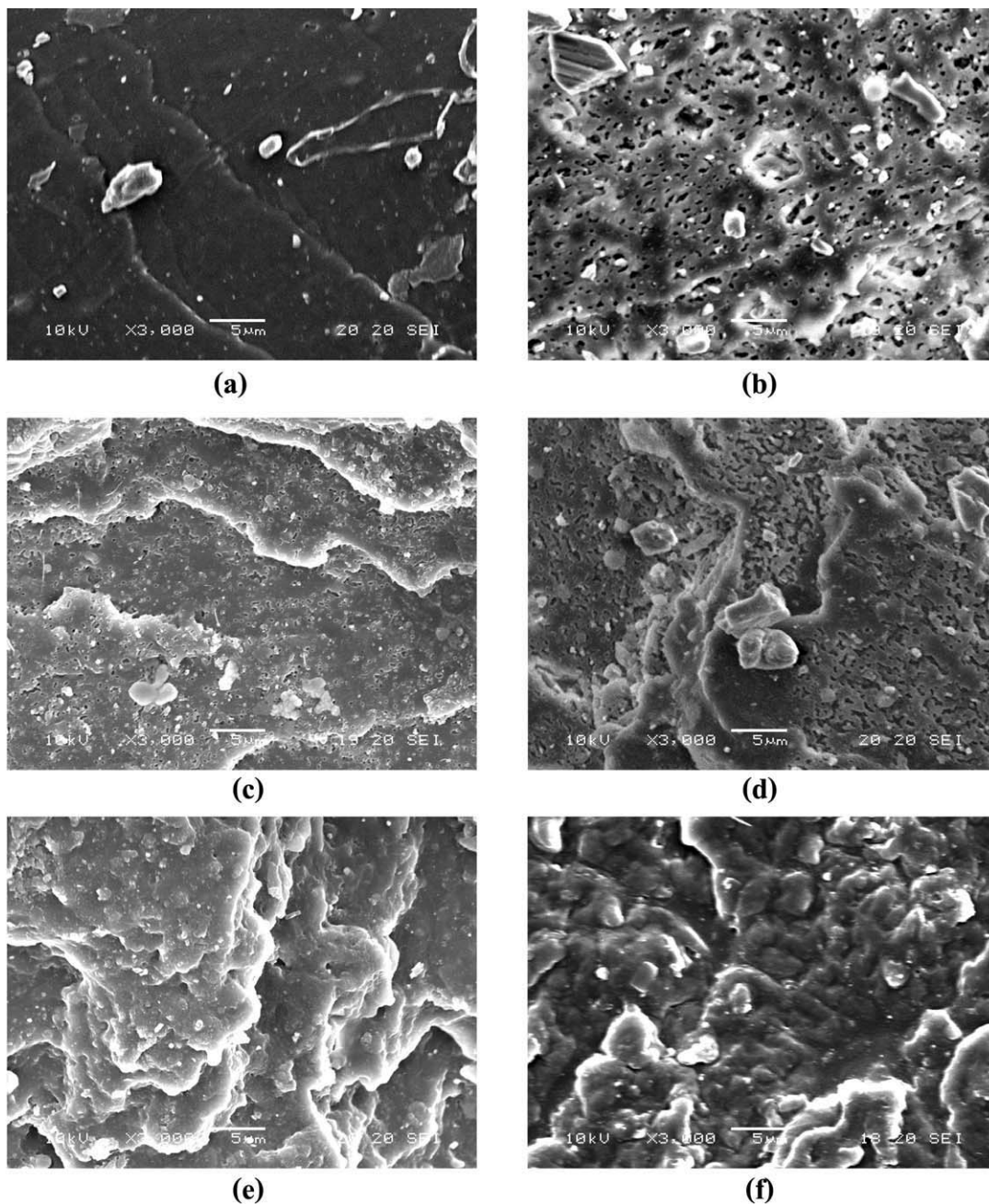
Figure 9 SEM micrographs of the (a) unfilled NR compounds and (b) LKD, (c) stearic acid coated CaCO$_3$, (d) ground CaCO$_3$, (e) silica, and (f) carbon-black-filled NR compounds after tensile fracture at 30-phr filler loading (3000×).

the hardness was even more pronounced in the systems filled with carbon black, which gave a harder material than silica because of its stronger adsorptive bonds. Arayapranee and Rempel[14] also reported similar filler-type influences on the Young's modulus and hardness.

Morphology

The morphology of the unfilled and filled NR compounds at 30-phr filler loading after tensile fracture is shown in Figure 9. The surface of the unfilled NR

compounds was smooth [Fig. 9(a)]. For the fracture surface of the NR compounds filled with CaCO$_3$ substances [Fig. 9(b–d)], the separation at the edge of the particle–matrix interface could still be observed in the cubical shape of the NR compounds filled with CaCO$_3$; this led to void formation. The aggregation of LKD resulted in an inhomogeneous distribution and, hence, weakened the interaction between the filler and the matrix. Aggregation caused defects within the compound because of the presence of voids between the particles and the matrix. This suggested that aggregates caused weak

points in the compound material; these could have led to undesirable material properties because of poor adhesion. This subsequently reduced the mechanical properties of NR compounds filled with $CaCO_3$ substances. $CaCO_3$ is considered to be a chemically inert filler when incorporated into polymers, in which the filler/matrix interfaces are weak. In the polypropylene/$CaCO_3$ composites, microvoids around the particles were obtained; this led to the deterioration of the composite properties.[23,24] For NR compounds containing a reinforcing filler, as shown in Figure 9(e,f), the fracture surface of the reinforcing filler showed a more homogeneous phase dispersion, and this resulted in a higher tensile strength. As shown in Figure 9, the morphology of the LKD-filled NR compound was more like those of the compounds filled with ground and stearic acid coated $CaCO_3$ than those filled with silica and carbon black. Thus, reinforcing particles showed a phase continuity in the compound that was better than that displayed by particles of $CaCO_3$ or LKD. As shown in Table II, silica and carbon black showed a high surface area; this resulted in more contact area between the filler and the matrix. Therefore, good adhesion and bonding existed between the filler and the matrix and showed a phase continuity in the compound; this provided a positive reinforcement effect for NR compounds containing a reinforcing filler. The SEM photomicrographs shown in Figure 9 confirmed that a larger surface area of the filler provided a better filler dispersion and interfacial bond between the filler and rubber matrix. This might have increased the strength of the compound. These observations were in agreement with the mechanical properties.

CONCLUSIONS

The purpose of this study was to explore the possibility of the use of LKD as an alternative filler for NR. The incorporation of fillers in NR compounds decreased t_{90} with increasing LKD, stearic acid coated $CaCO_3$, ground $CaCO_3$, and carbon black loadings in NR compounds, whereas silica showed a different trend in t_{90}, with t_{90} tending to increase with increasing silica loading. The Mooney viscosity increased with increasing silica and carbon black loading, whereas LKD and commercial $CaCO_3$ caused small changes in this property. At a similar filler loading, LKD showed the lowest viscosity followed by ground $CaCO_3$, stearic acid coated $CaCO_3$, carbon black, and silica. The filler loading and filler type influenced the processability of the rubber materials. The results indicate that the LKD-filled NR compounds offered processing advantages over the commercial fillers. The positive changes in the tensile and tear strengths, Young's modulus, and

hardness were quite significant with increasing loading of silica and carbon black in the NR materials. The tensile strength for NR filled with LKD showed a decrease with increased loading of LKD, whereas for NR filled with coated $CaCO_3$ or ground $CaCO_3$, an increase in the tensile strength was observed with low loadings (10–30 phr); this was followed by a decrease at higher loadings. The tear strength for NR with LKD decreased with the addition of LKD, whereas it showed little change (only a slight decrease) when coated $CaCO_3$ or ground $CaCO_3$ was used as a filler. For NRs containing $CaCO_3$-based fillers, the Young's modulus and hardness increased slightly as the loading increased. Silica and carbon black provided better mechanical properties than $CaCO_3$, mainly because of their high surface area and surface activity. Even with LKD having a larger surface area than both commercial $CaCO_3$ fillers, the mechanical properties of the LKD-filled NR compounds were lower than those of NR compounds with both coated and ground $CaCO_3$. SEM on the fracture surface showed poor filler dispersion and weak filler–matrix interaction in the LKD-filled NR materials. In fact, silica and carbon black particles were better embedded in the NR matrix than were LKD and other $CaCO_3$-based fillers. This helped explain the reductions in the tensile and tear strengths with LKD-filled NR materials. Although, from the overall mechanical properties, it could be suggested that the LKD-filled NR compounds had a poorer reinforcing ability than the silica- and carbon-black-filled NR compounds, one may still consider the use of LKD as a nonreinforcing filler in the rubber industry for economic and ecological reasons.

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