Morphologies of Natural Rubber/Gelatinized Starch and Mineral Clay Composite

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ABSTRACT

Morphologies of natural rubber/ cassava starch and montmorillonite clay composite were studied. Composites were prepared in a latex state and subsequently cast into films. It was found that starch dispersed at molecular level in rubber matrix in amorphous (gel) state. The tensile fracture surface of composites as revealed by scanning electron microscope (SEM) showed no trace of starch granules. Microstructural characterization of clay dispersed in rubber matrix using X-ray diffraction technique (XRD) revealed an absence of diffraction peak originated from the orderly stacked layers of clay. This suggested that the primary clay particles were dispersed into individual layers. The dispersed clay platelets provided more surface area for the rubber and starch interactions which resulted in better reinforcing and improved mechanical properties namely increased tensile strength, modulus, toughness, tear strength and hardness while sacrificing the ultimate elongation, comparing to a neat rubber.
Key words: natural rubber, gelatinized starch, montmorillonite clay, composite, morphology

INTRODUCTION

Natural rubber is one of the major economic crops of Thailand. Nowadays Thailand is in the position of the biggest rubber producer and biggest rubber exporter in the world. However, 90% of the rubber has been exported as raw materials such as sheets and latex concentrate, while only 10% is for local use. Other than exporting the raw rubbers, increasing domestic consumption by the development of the rubber end use products should be encouraged in order to increase the value added products of natural rubber. Therefore, more researches and developments of natural rubber are crucial to carry out in order to improve the properties of rubber products and to create the new rubber products. Natural rubber is an elastomeric material which consists of naturally occurring 1,4-polyisoprene. Due to its highly elastic character, natural rubber can easily undergo very large, and reversible elongation at relatively low stress. For most purposes, the strength of rubber is obtained via the crosslinking and the incorporation of reinforcing inorganic fillers, such as carbon black, silica and calcium carbonate.

The use of filler has played a vital role in rubber industry. Reinforcing fillers such as carbon black and silica greatly improve the properties of the rubber product, e.g., tensile strength, modulus, abrasion and tear resistance. Starch is a natural polymer and has been

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potentially used as a biodegradable material due to an attractive combination of availability, price, performance and being renewable. Recently, the composites based on nano-scale clay mineral fillers to enhance the thermal, mechanical and processing properties of the products have been interesting (Giannelis *et al*., 1999; McGlashan and Hally, 2003; Chiou *et al*., 2005). These materials are obtained by the dispersion of layered filler in a polymeric matrix. The most commonly used layered silicates are those of the smectite group. One of these is montmorillonite clay, which is widely used due to its high surface area (750 m^2g^{-1}) and large aspect ratio (greater than 50) according to Moore and Reynolds (1997). Montmorillonite differs from other used fillers such as talc, mica, and kaolin since its layered silicate can be dispersed into individual layers with only 10 Å thick. The dispersed platelets provide more surface area for interaction between phases.

Previous study on the mechanical properties of the rubber/starch and clay composite films (Tantatherdtam and Sriroth, 2006) prepared with various compositions has evidently demonstrated the reinforcing effect of starch and clay on the rubber matrix. The aim of this study was therefore to examine the morphological property of the composite system which is one of the important properties in determining the properties of composite materials. Wide angle X-ray diffraction (WAXD) was used to evaluate the interaction extent between clay filler, starch and rubber. The composite microstructure was revealed via scanning electron microscope (SEM).

MATERIALS AND METHODS

1. Materials

Natural rubber latex was supplied by the Thai Rubber Latex Corporation (Thailand) Co., Ltd. The low ammonia concentrated latex contains dry rubber content of 60.26%. The native cassava starch was obtained from SW Industrial Inc.,

Chonburi, Thailand. Cloisite® Na+, a natural montmorillonite clay, was supplied by the Southern Clay Products, Texas, USA.

2. Preparation of natural rubber-starch-clay composite

The composite films with total solid content of 30 grams were prepared from the latex aqueous mixture by casting. Granular starch was dispersed in distilled water (3% w/w) in concentrations of 5%, 10% and 15% w/w with respect to dried weight of rubber in the latex. To this respective proportion of starch suspension, clay (1 and 3 % w/w on a dry basis of rubber) was added and stirred for 20 minutes. This suspension was then heated at 95°C for 25 minutes until became transparent and was allowed to cool to room temperature. The starch paste/ clay mixture and the rubber latex were mixed and stirred vigorously for 30 minutes. The mixture was subsequently cast on the teflon framed with controlled thickness about 0.5 mm. and allowed to dry at room temperature for 48 hours and dried in an oven at 50°C for 18 hours.

3. Measurement and characterization

Tensile fracture surface of the composite films sputtering coated with gold were studied with scanning electron microscope (SEM) operated at 10 kV. X-ray diffraction (XRD) analyses were carried out on a JEOL model JDX 3530 using a Cu target, 30 kV and 40 mA with a scan rate of 3°/min.

Composite films were cut into dumb-bell shaped specimens for stress-strain test. Measurement was performed on the Autograph universal tester AGS-J series (Shimadzu) according to the ISO 37-1994(E) with a crosshead speed of 500 mm/min and a guage length of 20 mm. The test provided the ultimate tensile strength, the strain or elongation at break, the secant modulus e.g. 500% modulus (modulus at 500% strain), elastic or Young's modulus and toughness.

The value reported was the average of six measurements.

Tear strength was tested on the angle test pieces according to ISO 34. The tearing force is applied by means of a tensile testing machine with a constant rate of separation of the grips of 500 mm/min. Tear strength is the maximum force required to cause a rupture divided by the thickness of the specimen. Hardness was measured on a Model 716 Shore durometer type A according to ASTM D2240. Five measurements of hardness were made at different positions on the specimen of at least 6 mm in thickness.

RESULTS AND DISCUSSION

1. Mechanical properties

The results related to the modulus, ultimate tensile strength, elongation at break, hardness and tear strength were previously presented (Tantatherdtam and Sriroth, 2006) and summarized in Table 1. It can be seen that the mechanical properties of composite films increased considerably with an increase of starch and clay content. The mechanical behavior of composite can be characterized by its stress-strain properties as shown in Figure 1. The stress-strain curve of natural rubber shows a typical elastomeric behavior having low modulus and strength with high elongation. It was evident that with the addition of small amount of montmorillonite clay (1 and 3%) and starch (5 and 15%) to the rubber latex, the tensile strength (maximum stress) and modulus (slope of the initial portion) significantly increased while the elongation (strain) at break decreased. Composites became more rigid exhibiting higher resistance to deformation or high moduli, whereas they underwent smaller elongation before rupturing. The toughness follows the same trend as modulus and tensile strength, that is, an area under the stress- strain curve increased with increasing starch and clay contents. The results indicated the reinforcing effect of starch and clay to enhance the mechanical properties of the composite. Generally, the properties of composite materials are influenced

Table 1 Mechanical properties of natural rubber and natural rubber/gelatinized starch and montmorillonite clay composites (average value and standard deviation (in parentheses)).

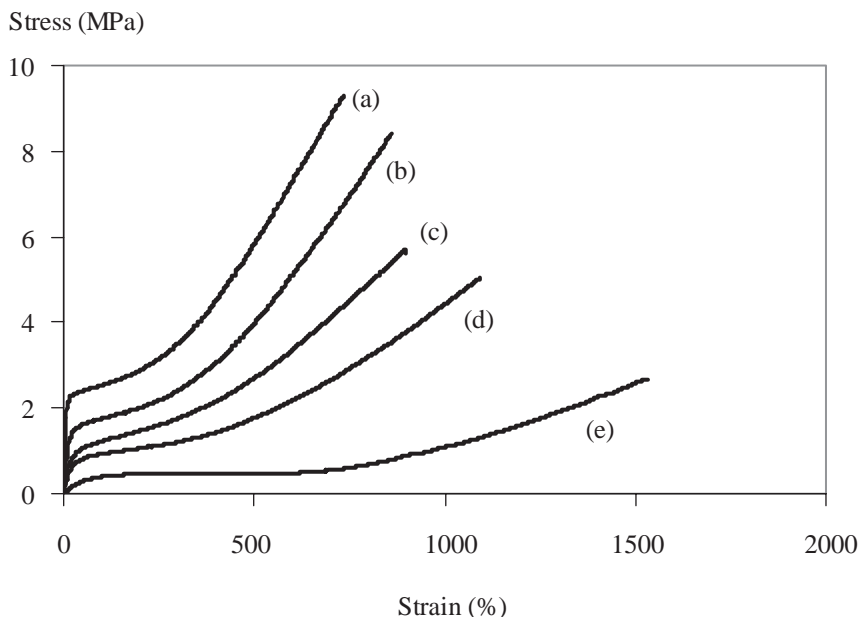|		Tensile strength (MPa)	Elongation at break (%)	500% modulus (MPa)	Young's modulus (MPa)	Tough-ness (MPa)	Shore A hardness	Tear strength (N/mm)
	Rubber film	2.7	1530	0.48	0.006	1616	23.0	6.9
		(0.1)	(109)	(0.01)	(0.001)	(160)	(0.4)	(0.1)
5% starch	1% clay	5.0	1090	1.86	0.037	2388	38.2	13.4
		(0.5)	(76)	(0.08)	(0.002)	(339)	(1.8)	(1.7)
	3% clay	5.7	897	2.67	0.057	2361	52.7	17.1
		(0.4)	(98)	(0.27)	(0.007)	(227)	(0.9)	(3.3)
10% starch	1% clay	6.6	998	2.92	0.058	3034	53.7	18.6
		(0.4)	(48)	(0.11)	(0.005)	(311)	(1.5)	(1.1)
	3% clay	7.9	768	4.26	0.084	2823	61.9	24.7
		(0.7)	(35)	(0.14)	(0.002)	(347)	(2.5)	(2.0)
15% starch	1% clay	8.4	860	4.03	0.105	3246	67.7	27.2
		(0.4)	(58)	(0.12)	(0.005)	(256)	(2.9)	(3.1)
	3% clay	9.3	734	5.98	0.218	3136	76.9	30.0
		(0.3)	(36)	(0.27)	(0.015)	(233)	(3.6)	(3.4)

Stress (MPa)

Figure 1 stress-strain curve of composites of natural rubber containing (a) 15% starch with 3% clay
(b) 15% starch with 1% clay (c) 5% starch with 3% clay (d) 5% starch with 1% clay and (e)
neat rubber.

by the properties of the components, the geometry of the filler phase (size, shape and size distribution), the nature of the interface between the phases, and the morphology of the system (Nielsen and Landel, 1994). It is therefore worth to examine the morphology of the composite system studied.

2. Microstructure study by scanning electron microscope (SEM)

Figure 2 shows SEM images of the tensile fractured surface of the composite samples, natural rubber film and the rubber film containing starch powder. The cassava starch granules were readily observed in the rubber film which was directly blended with the starch powder (Figure 2(b)). A round shaped starch granules were found with an average size of 10 μm. An absence of the starch granules in the composite film suggests that starch dispersing in the rubber matrix is completely in the amorphous (gel) phase (Figure 2(c) and (d)). This means that starch was completely gelatinized and highly destructured. In addition, the micrograph illustrates the existence of cell structure throughout the rubber film which can be clearly seen in Figure 2 (e) and (f). This was likely due to retrogradation of amylose molecules that leach out from starch granules during gelatinization and reassociate through hydrogen bonding upon cooling. The formation of these three dimensional amylose network was presumably reinforced the rubber matrix leading to the composite structure with high strength and stiffness. Miller *et al*. (1973) was long ago reported the function of exudate from the starch granule (soluble starch) which forms junction zones or hydrogen bonding when a paste is cooled to form a gel. They also showed the filamentous structure due to aggregation of amylose molecules on cooling after heating which were observed in the exudate from wheat, potato, and waxy maize starch. Han and Hamaker (2000) examined the microstructure of corn starch paste and gel with changing amount of soluble starch. Cold stage

SEM of gels revealed a fibrous structure with soluble starch while gels of insoluble starch alone showed a more cellular structure (starch ramnant). They also indicated the importance of leached amylose in gel strength.

3. Morphology by wide angle X-ray diffraction (WAXD)

Due to the periodic arrangement of the silicate layers of clay, the X-ray diffraction was used to characterize the orientation and
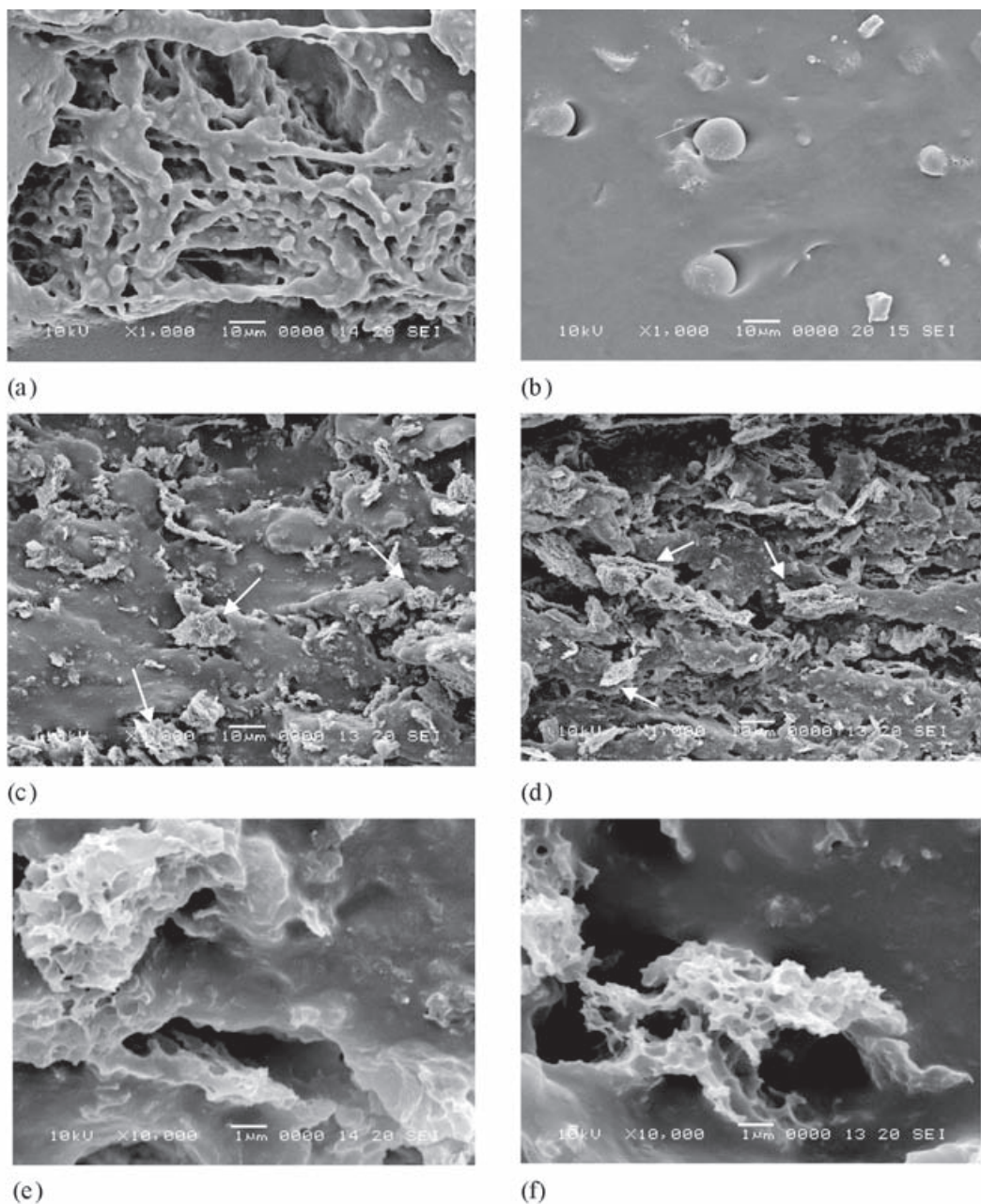

(a)

(b)

(c)

(d)

(e)

(f)

Figure 2 Tensile fracture surface by SEM of (a) natural rubber film (b) starch granule in rubber film (c) rubber-5%starch-1%clay composite film (d) rubber-5%starch-3% clay composite film (e) and (f) rubber-5%starch-3% clay composite film (× 10,000).

arrangement of clay structure. The startling property of montmorillonite is its ability to expand and contract its interlayer structure, exposing a large active surface area, and allowing polymer molecules to enter into the gallery. Due to the relatively weak force between the interlayer, an extended single polymer chain can move into the gallery spacing and, as a result, the distance of the layer between the clay platelets increases. This process is called "intercalation". "Exfoliation" or "delamination" occurs when the silicate layers (1 nm thick) are substantially expanded and no longer parallel. This leads to the separation of the individual clay layers dispersed in a continuous polymer matrix. It has been demonstrated that fully exfoliation into single individual clay platelets yields the excellent mechanical properties (Varghese and Karger, 2003; Wu *et al.*, 2004).

The X-ray diffraction patterns of natural rubber, montmorillonite clay, composite containing 5% starch with 1% clay and 3% clay, respectively are presented in Figure 3. A broad amorphous hill of natural rubber was clearly observed (Figure 3(a)). While the diffraction peak of pure clay appeared at 7.65 degree 2θ

corresponds to the silicate gallery spacing of 11.5 Å (Figure 3(d)). It was found that the XRD profiles of composite containing 5% starch with 1% clay and 3% clay, respectively (Figure 3(b) and (c)) exhibited no diffracted peak originated from the orderly stacked clay structure. This suggested that the ordered stacked layers of clay were probably either intercalated by the rubber and starch molecules or separated further apart and became dispersed as an individual platelet in the rubber matrix. The clay exfoliation in the rubber matrix provided more active surface area for the interaction between phases resulting in the enhanced composite mechanical properties.

CONCLUSION

It was shown that with incorporation of only small amount of clay (1 and 3%) and starch (5%, 10% and 15%) into natural rubber, the composite showed significant improvement in mechanical properties namely increased tensile strength, tensile modulus, toughness, tear strength and hardness when compared to the neat rubber. The tensile fracture surface examined by SEM
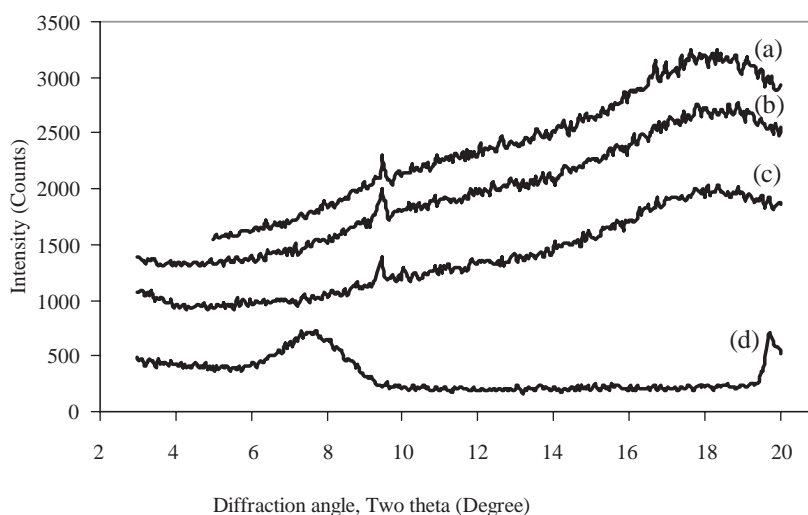

Figure 3 X-ray diffraction pattern of (a) natural rubber film, (b) rubber/5%starch/1%clay composite film, (c) rubber/5%starch/3% clay composite film, and (d) montmorillonite clay.

suggested that starch (amylose) molecules which were leached out from starch granules during gelatinization reassociate or realign through hydrogen bonding upon cooling. The formation of these three dimensional amylose network was presumably reinforced the matrix leading to the composite structure with improved mechanical properties. A fully exfoliated clay structure in the rubber matrix as confirmed from the disappearance of orderly stacked clay structure peak in XRD diffraction profile gave rise to the nanometered scale filler and hence enhanced reinforcing effect.

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