Effects of Poling on Electrical Properties of Flexible Piezoelectric Composites with Natural Rubber Matrix

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Abstract. This work was done to study effects of electrical applied voltage on electrical properties of flexible piezoelectric composites with natural rubber (NR) matrices. Different amounts of lead magnesium niobate titanate (PMNT) as a piezoelectric phase were added into NR matrices. NR/xPMNT (where x = 0, 60, 80, 100, 120 and 150 phr) composites were consequently obtained. The composites were poled under 25 kV/cm electric field for 30 mins. For all the samples, tetragonality is enhanced after poling. Dielectric and ferroelectric properties, and generated electrical voltage of unpoled and poled samples were measured. For the samples with x ≤ 80 phr, the properties are not improved with the poling process. However, for x > 80 phr samples, the properties are significantly enhanced after poling. A percent increase in generated electrical voltage after poling tends to increase with increasing PMNT concentration. The overall result suggests that the NR/100PMNT composite is suitable for applications as high mechanical damage resistance piezoelectric sensors and generators.

Keywords: Piezoelectric composite, Natural rubber, PMNT, Energy harvesting

1. Introduction
Piezoelectric material is a type of smart materials that plays an important role in the technology development in the past several decades. It has been widely used as piezoelectric generators, sensors, actuators, and transducers for a wide range of applications such as hard disk drive, vehicle, medical instrument industries and etc. [1-4]. Among these applications, piezoelectric sensors and actuators have been mostly received much attention for a continuous development to reach their properties to the requirement. From searching for new piezoelectric/ferroelectric materials, lead magnesium niobate titanate [Pb(Mg¹/₃Nb²/₃)O₃₋ₓTiₓO₃], had been invented. It was found that the material with x = 0.30-0.35 exhibited excellent electromechanical properties i.e. an extreme high piezoelectric coefficient (d₃3 = 600 pC/N) and a high electromechanical coupling factor (kₚ = 0.7) [5, 6]. Because of its attractive piezoelectric properties, the material has been selected to use as piezoelectric sensors and actuators. However, in actual applications, they often crack and eventually fail after a large
cycling number of electrical or mechanical loads is applied. This is due to a high brittleness of the materials. To solve this problem, many research investigating about the fabrication of piezoelectric materials with high mechanical failure resistances have been done. Most of them has fabricated piezoelectric materials in forms of composites, having high mechanical failure resistances [7-9]. In the preparation of flexible piezoelectric composites, piezoelectric materials were embedded in various types of polymers such as polyurethane [10, 11], epoxy [12, 13], polydimethylsiloxane [14] and polyvinylidene fluoride [15, 16]. Natural rubber (NR) has been an important economic plant of Thailand for a long time. Because its excellent mechanical properties such as a high toughness and a high elongation at break, it is selected as a subject for a wide range of applications [17]. Due to the high mechanical toughness, in this research, natural rubber was used as the matrix phase of piezoelectric composites with Pb(Mg1/3Nb2/3)O3Ti0.35O3 (PMNT) particles as the dispersed phase. It is well known that for piezoelectric materials, their piezoelectric properties are enhanced after a high electric field is applied [18, 19]. Based on reviewing literature, there are no research studying electrical poling on piezoelectric composite with NR matrix.

Therefore, in this study, in the first step, NR/PMNT (when x = 60, 80, 100, 120 and 150 phr) flexible piezoelectric composites were fabricated. The composites were then electrically poled under a high electric field. Significant electrical properties, i.e. dielectric and ferroelectric properties, and voltage generation performance, of unpoled and poled samples were measured and comparatively analyzed. The result shows that the properties of the composites with high PMNT content were enhanced after poling. The observed result is then discussed and explained in detail. We hope that this research study can develop a new flexible piezoelectric material suitable for piezoelectric sensor and generator applications.

2. Experimental method
Pb(Mg1/3Nb2/3)O3 powder modified with ZnO was prepared by a columbite route technique. MgNb2O6 (columbite) powder was firstly synthesized by using MgO (99%, TOPLUS, China) and Nb2O5 (99.99%, TOPLUS, China) precursors. MgNb2O6 powder was then mixed with the predetermined amounts of PbO (99.5%, TOPLUS, China), TiO2 (99%, TOPLUS, China) and ZnO (99.7%, TOPLUS, China) powders. The mixture was calcined at 900°C for 5 hr. Different amounts of PMNT powders were added into natural rubber (NR) matrices by using an internal mixer (Rheomix OS, Thermo Scientific, USA) to prepared NR/PMNT (where x = 60, 80, 100, 120 and 150 phr, which are equivalent to 38, 44, 50, 55 and 60 wt%, respectively) mixtures. NR/PMNT composites with 1 mm thickness were formed by using a compression molding under a 2500 psi pressure at 150°C. The NR/PMNT composites were poled under an electric field of 25 kV/cm for 30 min at 60°C. Phase, microstructure and chemical composition were characterized by an X-ray diffraction technique (XRD, Rigaku SmartLab, Japan), a scanning electron microscope (SEM, JSM-IT300LV, JEOL, Japan) and energy dispersive X-ray spectrometer (EDX, JSM-IT300LV, JEOL, Japan), respectively. Dielectric and ferroelectric properties, and generated voltages were measured by an LCR meter (GW Instek, LCR-821, Taiwan), a Sawyer-Tower circuit, and an oscilloscope (Rigol, DS1052E, USA), respectively. Effects of the electrical poling on the properties of the composites were demonstrated and discussed.

3. Results and discussion
Figure 1 shows XRD patterns of the composites with 60, 120 and 150 phr PMNT before and after poling. The main peaks (unlabeled peaks) are belonged to a perovskite phase of Pb(Mg1/3Nb2/3)O3Ti0.35O3 which corresponds to ICSD file no. 159255. It is found that the reflections of pyrochlore, ZnO and unknown phases are also appeared in the XRD patterns of all the unpoled samples. It is believed that the observed pyrochlore phase is formed during PMNT preparation process, at which PbO preferably reacts with Nb2O5 [20], while ZnO is an additive compound of NR. The unknown phase is possibly formed from an interaction between chemical ingredients composing in the NR material. However, the unknown phase peak disappears after the samples are poled.
Enlarged views of peaks at $2\theta \approx 45^\circ$ of corresponding patterns are shown in Fig. 1(b). For each sample, the peak is obviously split after poling. Moreover, it can be seen from the result that the ratio of the intensity of (002) peak to that of (200) peak increases after poling. This indicates the increase in the amount of the (002) plane orienting its direction parallel to the X-ray beam which is perpendicular to the sample’s surface (electrodes). It is know that for a tetragonal ferroelectric an electrical polarization directs along $c$ axis which is parallel to the (002) plane direction. That means that the number of the electrical polarization aligning perpendicular to sample’s surface increases after poling. However, the peak intensity ratio does not change with the variation of PMNT content. The change of crystal orientation can result in an enhancement of electrical properties of the composites which will be discussed later.

![Image](image.png)

**Figure 1.** (a) XRD patterns before and after poling of composites with 60, 120 and 150 phr PMNT. Unmarked peaks are belonged to a perovskite phase. (b) Enlarged view of the diffraction peak at $2\theta \approx 45^\circ$. The peaks of (b) are corresponded to those of (a).

The chemical compositions of NR/PMNT composites were measured by mean of energy dispersive X-ray spectroscopy (EDX) technique. In this experiment, the fracture surfaces of samples after tensile testing were examined. The EDX spectrum of NR/100PMNT composite is shown in Fig. 2. The observed particle contains Pb, Mg, Nb, Ti, Zn and O elements. This confirms that the presented particles are PMNT piezoelectric materials which well distribute and partially agglomerates in NR matrix. It can also be seen from the figure that the NR matrix possesses micro-voids. These voids are possibly created from pulling out of PMNT particles during the tensile testing. From the observation of microstructure of composites (the result do not show here), the amount and the size of voids increase with increasing PMNT content. This reveals that a large amount of the dispersed phase degrades the bonding performance between them and the matrix phase.
Figure 2. A chemical composition by mean of energy dispersive X-ray spectroscopy (EDS) technique of NR/100PMNT composite.

Figure 3(a) shows the plots of dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) measured at room temperature at 200 kHz as a function of PMNT content of unpoled and poled NR/PMNT composites. It can be seen from the result that the $\varepsilon_r$ and tan$\delta$ of an unpoled NR are found to be about 3.3 and 0.07, respectively, which are consistent with the previous result reported in Ref [21]. The properties of the NR are degraded, i.e. a decrease in $\varepsilon_r$ and an increase in tan$\delta$, after poling. The NR sample was seemed to be burnt after the high poling field was applied. It is believed that mobile charges included in the NR material, acting as charge carriers, conduct an electrical current through the NR bulk [22]. This causes the degraded dielectric properties after poling of the material. For the composites with $x = 60$-80 phr, $\varepsilon_r$ and tan$\delta$ do not change after poling. However, for the composites with the PMNT content greater than 80 phr, the $\varepsilon_r$ obviously develops after poling while the tan$\delta$ does not change. For both unpoled and poled samples, the $\varepsilon_r$ of the samples tends to increase with increasing PMNT content. This is due to the domination of the PMNT phase which possesses higher $\varepsilon_r$ as compared to the NR phase. This causes the increment of $\varepsilon_r$ of the composites. For the composites with large amounts of PMNT additions (> 80 phr), it is believed that the mobile charges, migrating under the applied field, are trapped at interfaces between PMNT and NR phases. The trapping process is consistent with that proposed in the previous work studied by Ortiz-Serna et al. [23]. Moreover, the charge carriers could be trapped by space charges produced from the PMNT phase. For piezoelectric materials, space charges in forms of cation and oxygen vacancies, which are electrically negative and positive, respectively, can be formed [24]. This contributes to the reduction of electrical conductivity of the composites, which is corresponded to the less value of tan$\delta$. Meanwhile, the $\varepsilon_r$ of the composites is improved.

Remanent polarization ($P_r$) and coercive field ($E_c$) measured before and after poling are plotted as a function of PMNT content as shown in Fig. 3(b). The properties were measured at room temperature and at 25 Hz. For the composites with $x \leq 80$ phr, $P_r$ does not change after poling. As $x$ is beyond 80 phr, the $P_r$ apparently develops after the composites are poled. For all the composites, the $E_c$ is enhanced after poling. The enhancement of $P_r$ of the composites is attributed to the de-aging effect. Generally, for ferroelectric materials containing charged defects, i.e. cation and anion vacancies, these defects can form defect dipoles. The stabilization of the alignment of defect dipoles in ferroelectric materials increases with time. This causes the decrease in $P_r$ and $E_c$ of the materials [25]. It is known that an aging state of a ferroelectric material is practically recovered, called a de-aging process, by a thermal annealing or an application of an appropriate electric field [26]. Although aging effect is dominated in ferroelectric materials in the form of ceramics, however, in this research, it is believed that the aging process also has a significant effect on ferroelectric particles.
Figure 3. (a) Room temperature dielectric constant and loss tangent measured at 200 kHz and (b) remanent polarization and coercive field before and after poling of NR/PMNT composites.

Table 1. The generation of voltage of NR/PMNT composites under a 300 N impact load.

| PMNT content (phr) | Open-circuit output voltage (V) | % increase in output voltage after poling |
|--------------------|--------------------------------|------------------------------------------|
|                    | Before poling                  | After poling                             |
| 0                  | 0.24 ± 0.02                    | 0                                        |
| 60                 | 0.89 ± 0.07                    | 1.08 ± 0.13                              | 21 |
| 80                 | 0.93 ± 0.05                    | 1.68 ± 0.15                              | 81 |
| 100                | 1.61 ± 0.05                    | 2.42 ± 0.19                              | 50 |
| 120                | 0.98 ± 0.04                    | 2.07 ± 0.06                              | 111|
| 150                | 0.71 ± 0.03                    | 1.97 ± 0.09                              | 177|

Average values of open-circuit output voltage generated under a 300 N impact load measured before and after poling of NR/PMNT composites are given in Table 1. The result suggests that the electric field application has a significant effect on the generation of output voltage of NR/PMNT composites. From the overall observed result, the enhanced electrical properties of NR/PMNT composites could be caused by the orientation of dipole moments inside the piezoelectric phase. From XRD result analysis, the amount of (002) plane orienting its direction to an applied field direction increases after the field is applied, as schematically shown in Fig. 4. A higher number of dipole moments remaining their directions in an applied field can promote a higher \( P_r \) of a ferroelectric. Subsequently, this is accompanied with a higher interaction strength between all the dipole moments in the material. A higher activation energy for the dipole moments to switch their directions is required, resulting in an increment of \( E_c \). This also contributes to a higher piezoelectricity of the poled samples. Generally, for \( d_{33} \) mode, at which electric charge is generated in direction 3 (polarization direction) when the material receives a mechanical force in the direction 3. Therefore, a ferroelectric with a higher number of dipole moments aligning in direction 3 possesses a greater electric charge when a similar force is applied. Moreover, an enhancement of the voltage production of poled samples could be partially caused from a trapping of mobile charges at phase boundaries and a de-aging effect. For the trapping effect, it causes a reduction of electrical conductivity materials which can promote a separation of generated positive and negative charges. This is supported by the decrease in dielectric loss of the PMNT-added samples. For the de-aging effect, a high electric field application promotes an ordering of dipole moments of ferroelectric materials [26]. These effects subsequently lead to the enhancement of piezoelectric properties of the NR/PMNT composites. A percent increment in the output voltage of composites tends to increase with increasing PMNT content, as shown in Table 1. It is reasonably believed that an increase in
piezoelectric phase content results in the enhancement of the piezoelectricity of the composites. It can be seen that the maximum output voltage was found in the poled NR/100PMNT composite. This makes the composite suitable for applications as piezoelectric sensors and energy harvesters.

![Figure 4. A schematic diagram showing the orientations of crystal structure of PMNT phase before and after poling. A blue arrow represents a direction of a dipole moment embedded in a unit cell (yellow cube). The applied field direction, which is perpendicular to the electroded-surfaces, is also shown.](image)

4. Conclusion
Flexible piezoelectric composites with a formula of NR/xPMNT (when x = 0, 60, 80, 100, 120 and 150 phr) were successfully fabricated. Dielectric and ferroelectric properties, and voltage generation performances of composites before and after poling were measured and comparative studied. The result shows that dielectric constant and remanent polarization of composites with x ≥ 100 phr are enhanced after poling while those of composites with x < 100 phr do not change after poling. For voltage generation of the composites with x ≤ 60 phr, their output voltage values do not change after poling while those of the others raise up after the composites are poled. For all the composites, the electrical poling causes the increase in the coercive field. In addition, the percent increase in the increase in output voltage after poling tends to increase with increasing x. The improvement of these electrical properties of the composites are explained in the terms of charge trapping effect, de-aging effect and increased degree of polarization ordering. We hope that this research study leads the development of a new flexible piezoelectric composite that is suitable for applications as piezoelectric sensors and energy harvesters.

Acknowledgment
This research was supported by Natural Rubber Innovation Research Institute, Prince of Songkla University (Grant No. SCI601093S).

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