Studies of ENR-25/TiO$_2$ Composites for Electronic Materials Packaging Applications

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Abstract. In this study, the synthesis and characterization of epoxidized natural rubber/ Titanium dioxide (ENR-25/TiO$_2$) composites in two different solvent (Toluene and Chloroform) via sonication technique was conducted using Fourier transform infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). Spectroscopy results showed new peak at 1662 cm$^{-1}$ for both ENR-25/Titania composite films, which is related to weak C-O stretching vibration. Moreover, The peak at 3390.4 cm$^{-1}$ and 3384.3 cm$^{-1}$ of the composites are produced by Ti-OH stretching vibration shifts. The composite with toluene solvent showed poor dispersion of TiO$_2$, which can be seen by the agglomeration embedded in the matrix. The composite with toluene solvent showed same trend of composite with toluene. The poor TiO$_2$ dispersion in the composite can be observed by the surface as bright layers. These layers appeared because the TiO$_2$ particles covered the surface of purified ENR-25 matrix.
1. Introduction

Nowadays, the electronic industry is increasing rapidly with smaller and better performance products to achieve advanced technology. Electronic packaging of microelectronics was known as the art of enclosing, cooling, powering, chip packaging, interconnecting, and protecting chips from the immediate surroundings environment as well as protecting the related immediate surrounding environment from the chips [1-6]. The electronic packaging of a system can be classified into different levels of packaging such as packaged chip, bare chip, electronic subassembly, printed circuit board assembly and electronic assembly to system or final electronic product. The aim of electronic packaging is to simplify and/or reduce the packaging levers number [7-11].

In current state, epoxy is used as a main material of the electronic material packaging to be medium for the most part in this application [12-14]. Nevertheless, epoxy contributes to the problem such as expensive and un-green material. Additionally, the use of epoxy (thermosetting matrix) also could cause other problem such as recycle difficulties, which in turn effect negatively on the environment. With increased performance requirements for smaller, more capable, and more efficient electronic systems, thermal challenges have become critical issues in electronic packaging design. Breakthroughs are required in board, advanced cooling solutions, practical design at chip and system package levels.

In response to these serious needs, advanced and new materials with process developments in packaging and cooling technology are needed to provide good-controlled thermal transient behavior, high thermal transfer efficiency, lightweight, environmental compatibility and low fabrication cost.

The use of epoxidized natural rubber as a polymer matrix will provide an alternative of epoxy-based polymer usage. Furthermore, the use of titanium dioxide as moieties in ENR-25 can improve the properties of the material [15,16], which in turn increase the opportunity of this combination to be used in electronic materials packaging applications.

Therefore, the aim of this research is to synthesize a new composite obtained from ENR-25 as a polymer matrix and Titanium dioxide (TiO2) as an inorganic filler for electronic packaging application. Furthermore, the structural and morphological properties of ENR-25/TiO2 composites were investigated in this work.

2. Experimental

2.1. Materials and chemicals

The elastomer (epoxidized natural rubber with 25% mole epoxidation) was obtained from Rubber Research Institute, Malaysia (RRIM). Titanium (IV) butoxide, 98%, Ti(OCH2CH2CH3)4 is a titanium alkoxide which commonly used as a source of titanium for the synthesis of Titania or titanium dioxide (TiO2) and it was purchased from Merck, Germany. While solvents such as 2-propanol (IPA), n-hexane, chloroform and toluene were purchased from Systerm Malaysia.

2.2. Measurements and characterization technique

FTIR spectroscopy: Transmission FTIR spectra of composite films were recorded from thin KBr disc of the samples with Perkin Elmer 2000 FTIR spectrophotometer at room temperature. The samples were scanned from 4000 to 400 cm−1 with resolution of 0.4 cm−1. By using FTIR, the functional groups in a molecule can be identified.

FESEM: The morphological features of each sample were obtained using a Zeiss Supra 35 VP field emission scanning electron microscopy (FESEM). The samples were prepared with gold coating for the measurements.

2.3. Synthesis of ENR-25/ TiO2 composites

First, 20 g of ENR-25 was dissolved in 400 mL of two different solvents (toluene and chloroform) separately and stirred for 24 h at 25 ºC temperature. The rubber solution was then filtered through cotton gauze to separate the high from the low molecular weight ENR-25. The latter was precipitated
in n-hexane while stirring using a glass rod. The white precipitate stuck to the glass rod was then transferred to a Teflon dish and dried in a vacuum oven at 60 °C temperature for two days. A 1.32 x 10^{-3} M (3.82 x 10^{-3} mg mL^{-1}) Titania precursor solution was prepared by diluting a 40 mg (1.32 x 10^{-4} mol) of precursor in 10 ml IPA. Both of the ENR-25 solutions obtained from subsection 3.4.2 were used.

In a typical preparation, 10 mL of Titania precursor solution was slowly added drop wise to the 40 mL of purified ENR-25 at room temperature. Upon completion, the mixture was continuously sonication for 10 minutes to make sure it is homogenously distribute into the ENR-25 solution for both toluene and chloroform respectively. The resultant reaction mixture was then cast onto Teflon dishes and dried in vacuum oven at 60 °C for two days to obtain ENR-25/TiO_2 composites as shown in Figure 1.

![Figure 1](image)

(a) (b)

*Figure 1. ENR-25/Titania composite film samples prepared with dissolution of ENR-25 in (a) toluene, and (b) chloroform.*

### 3. Results and Discussion

#### 3.1. FTIR analysis

Figure 2 presents the FTIR spectra of (a) purified ENR-25, (b) ENR-25/ TiO_2 composite in toluene, and (c) ENR-25/ TiO_2 composite in chloroform. The spectra of purified ENR-25 (Figure 2 a) indicate the presence of CH3, CH2, CH, epoxide and isoprene (C=C) [17]. The CH3 asymmetric and symmetric stretching is detected at 2963.6 and 2860 cm\(^{-1}\) respectively and CH2 asymmetric stretching at 2921 cm\(^{-1}\). The values mentioned are all listed in range of alkane groups, which is 2840 - 3000 cm\(^{-1}\) [18]. The CH3 at the 2963.6 cm\(^{-1}\) and CH2 at 2921 cm\(^{-1}\) are emerged as split peaks due to difference resonance for C-H stretching. Similar asymmetric and symmetric stretching of CH3 for both ENR-25/Titania composites at 2963.6 cm\(^{-1}\) and 2860 cm\(^{-1}\) were shown in Figure 2 (b) and (c) respectively. The peak at 3390.4 cm\(^{-1}\) and 3384.3 cm\(^{-1}\) were signature of hydroxyl group [19] in both ENR-25/Titania composite in dilution of (b) toluene and (c) chloroform samples respectively. Generally, there are no significant differences among the three samples except for the peak intensity of the characteristic peaks. The broad band presented at 1662 cm\(^{-1}\) for both ENR-25/Titania composite films is related to weak C-O stretching vibration.
According to Xu (2015), the peaks at 875 cm\(^{-1}\), 836 cm\(^{-1}\) and 1252 cm\(^{-1}\) belong to epoxy ring [20]. The peak at 3390.4 cm\(^{-1}\) and 3384.3 cm\(^{-1}\) are produced by Ti-OH stretching vibration shifts, which may be attributed to the effect of hydrogen bond.

3.2. FESEM morphology

The FESEM images of purified ENR-25 and ENR-25/Titania composites with toluene and chloroform solvent are shown in figure 3 a, b and c respectively. The purified ENR-25 shows a typically smooth surface. The small amount of impurities presented on the surface of the sample could be due to the dirt of surrounding which caused by negligence of handling the sample as the ENR-25 has a sticky characteristic [21,22]. Figure 3 (b) shows the surface of ENR-25/ TiO\(_2\) composite with toluene solvent. The non-homogenous dispersion of TiO\(_2\) can be seen by the agglomeration embedded in the matrix. Therefore, the surface seems swelled in the most parts of the sample due to the TiO\(_2\) agglomeration. Figure 3 (c) shows the surface of ENR-25/ TiO\(_2\) composite with chloroform solvent. The bright phase showed the dispersion of TiO\(_2\) particles. The TiO\(_2\) particles covered the purified ENR-25 matrix. The non-homogenous dispersion of TiO\(_2\) can be seen by the surface as bright layers. These layers appeared because the TiO\(_2\) particles covered the surface of purified ENR-25 matrix [23-25].
Figure 3. FESEM image of (a) purified ENR-25, (b) ENR-25/TiO$_2$ composite in Toluene (c) ENR-25/TiO$_2$ composite in Chloroform

4. Conclusion
The data obtained by FTIR measurements revealed the possible interaction of TiO$_2$ and ENR-25 in different dissolution solvent. The composite films were not hybrid due to the technique used to produce the ENR-25/TiO$_2$ composite and have been revealed by FESEM of the non-homogeneous dispersion of TiO$_2$ in ENR-25 matrix. The aggregation of TiO$_2$ nanoparticles into the ENR-25 matrix becomes severe in the purified ENR-25 dissolved in toluene compared with dissolved in chloroform.

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