The Influences of Zirconium Dioxide on ENR-25/ZrO2 Composites: FTIR and TGA Analysis

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Abstract. The characterization and thermal stability of purified epoxidized natural rubber with 25 mol% epoxidation (ENR-25) and treated epoxidized natural rubber with 25 mol% epoxidation / Zirconium dioxide (ENR-25/ZrO2) Composites were studied using Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA). The ENR-25/ZrO2 composites were treated with acetic acid and two different loading (50 and 100 mg) of ZrO2 were used to form the composites. FTIR results show the ester (C-O) peaks at 1000-1300 cm⁻¹ due to the presence of acetic acid in the composites. The disappearance of epoxide peak at range 880-875 cm⁻¹ indicated that ZrO2 have formed hybrid bonds with opened epoxide rings. The both ENR/ZrO2 composites showed 2 major thermal degradation steps (304 - 489°C and 493 – 551°C) for 50 mg ZrO2 loading and (306 - 497°C 512 – 581°C) for 100 mg ZrO2 loading indicating that the thermal stability of the composites have improved.

1. Introduction

Epoxidized natural rubber (ENR) is obtained from the chemical modification of natural rubber (NR). The ENR are characterized by having two or more epoxy units attached to NR molecule. ENR are produced by epoxidation process using peracetic acid of the NR latex [1-4]. Nowadays, the increasing interest of the people in science and technology regarding ENR makes it inevitable to understand the detail structure of ENR in term of epoxidation and physical form of rubber [5].

Even though ENR is the product from the modification process of NR, the characteristic of NR and ENR have no difference. There are a few unique characteristic of NR which including its glass transition temperature (Tg). The Tg of the NR shows that at low temperature, NR will have the glassy
characteristic while at high temperature; NR will have the rubbery characteristic [1,6]. In the meantime, zirconia (ZrO₂) recently has a high demand in most of the chemical based industry such as the dental industry. It has a supportive characteristic in which it improves the mechanical properties and biocompatibility of the fixed dental prostheses (FPDs) that is being used in implantation process in dental industry [7]. Pure ZrO₂ cannot be used at the high temperature because of large changes in volume from tetragonal to monoclinic phase. This will affect the elasticity and fracture limit of the ZrO₂, which will result in crack and flaws in ceramics. At the same time, ENR-50 has epoxy characteristics, which has the characteristics of low toughness and brittleness. So, with the brittle characteristic that ZrO₂ had, the toughness and brittleness of ENR-50 can be improved. The formation of covalent bond between ENR-50 and ZrO₂ will change its chemical properties and leads to produce a new hybrid. In this study, the characterization of the ENR-25 and ENR/ZrO₂ composites at different ZrO₂ were carried out using Fourier Transform Infrared Spectroscopy (FTIR), while their thermal stability were investigated using thermo gravimetric analysis (TGA). The experimental comprises purification of ENR-25, acid treatment of ENR-25 and the ENR-25/ZrO₂ composites synthesis.

2. Experimental

2.1. Materials
Epoxidized natural rubber, 25% mole epoxide (ENR-25) was obtained from Malaysia Rubber Research Institute (RRIM), Malaysia. Zirconium precursor, Zr(OCH₂CH₂CH₃)₄ was purchased from Fluka, USA. Acetic glacial 99.8% (CH₃COOH) was purchased from Hamburg Chemical, Germany. The solvents such as N-hexane, Tetra hydro furan (THF), Toluene and 2-propanol (IPA) were purchased from System, Malaysia. All the materials and chemicals used in this study were used without any additional purification unless otherwise stated.

2.2. Composites synthesis
In this study, the synthesis of composites gone through three main stages ENR-25 purification, ENR-25 acid treatment, and ENR-25/ZrO₂ composites synthesis at different ZrO₂ loading, 50 and 100 mg respectively (Figure 1).
To purify ENR-25, 20.00 g of ENR-50 was swelled and stirred in 400 mL of chloroform 25°C for 24 hours and then the solution was filtered through a cotton gauze pack to separate gel from sol content. The latter poured into n-hexane, Tetra hydro furan (THF), Toluene and 2-propanol (IPA) were purchased from System, Malaysia. All the materials and chemicals used in this study were used without any additional purification unless otherwise stated.

The acid treatment was carried out using 4 mL of glacial acetic acid added into rubber solution (200 mg Purified ENR-25 with 40 mL Toluene). The solution was refluxed and stirred at 110°C. After 3 hours, different Zr(OCH₂CH₂CH₃)₄ loading (50 and 100 mg) were added into the acid treated ENR-25 solution separately and refluxed at 60°C for 24 hours. The ENR/ZrO₂ solution was poured in Teflon dishes and air-dried before dried in vacuum oven at 50°C for 24 hours.
2.3. Composites characterization and analysis

FTIR analysis was carried out using Perkin-Elmer 2000- FTIR. About 100.00 mg of sample was placed onto zinc selenide (ZnSe) window using attenuated total reflection (ATR) method. The sample was scanned at range 4,000 cm\(^{-1}\) to 650 cm\(^{-1}\) with 16 numbers of scans.

The thermal stability of the samples was conducted using thermal gravimetric analyser (Perkin Elmer TGA-7). The samples were heated under nitrogen gas start from 30 °C to 900 °C. The heating rate was 20 °C min\(^{-1}\) in all cases.

2.4. Purified ENR-25 characterization

The FTIR spectrum of purified ENR-25 is shown in Figure 2. Generally there are five functional groups that represent the chemical structure of purified ENR-25. There are CH3, CH2, CH, epoxide and isoprene (C=\_C). The CH3 asymmetric at 2964 cm\(^{-1}\), symmetric stretching at 2860 cm\(^{-1}\) and CH2 asymmetric stretching at 2925 cm\(^{-1}\) are observed clearly.

These values are between 3100 and 2750 cm\(^{-1}\). The CH3 at 2964 cm\(^{-1}\) and CH2 at 2925 cm\(^{-1}\) appeared as split peaks due to difference resonance for C-H stretching [1,8]. At low wavenumber, the peak at 1450 cm\(^{-1}\) corresponds to both CH3 and CH2 bending vibration and at 1378 cm\(^{-1}\) for C-H bending vibration.

The existence of the epoxide ring in the purified ENR-25 is shown by peak at 875 cm\(^{-1}\) due to half ring stretching of the epoxide while the full ring stretching is at 1234 cm\(^{-1}\) [9]. The C=C band of the isoprene is shown at 835 cm\(^{-1}\) [6,7] as a shoulder peak to the epoxide.
3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy
Figure 3 shows the FTIR spectra of ENR-50/ZrO$_2$ composites at 50 and 100 gm of ZrO$_2$ loading. Generally, the composites produced few new peaks that are observable in FTIR. The peak of C=O stretching vibration at 1735.2 cm$^{-1}$. The peak region at 1000-1300 cm$^{-1}$ is assigned to the ester (C-O) functionalities due to the presence of acetic acid in the composites. In this band, the intensity to have two or more bands is probable i.e. two adjoining band within this range. Nevertheless, the band depletion also occurs throughout the process. The half ring stretching of the epoxide at range 880-875 cm$^{-1}$ is disappeared as ZrO$_2$ added. This indicated that ZrO$_2$ has formed hybrid bonds with ring opened epoxide units. The broad peak 3400-3450 cm$^{-1}$ indicated the existence of the OH group of that originates from precursor intermediate (Zr-OH) via its stretching vibration mode [10,11].

Figure 2. FTIR spectrum of the purified ENR-25

Figure 3. FTIR spectra of ENR-25/ZrO$_2$ composite at (a) 50 mg and (b) 100 mg of ZrO$_2$ loading.
3.2. Thermo Gravimetric Analysis

The TG thermograms of purified ENR-25 and ENR-25/ZrO$_2$ composite at different ZrO$_2$ loading are shown in Figure 4. TG thermograms of purified ENR-25 show a single step degradation range at 382 - 466 °C [12]. While both ENR/ZrO$_2$ composites showed 2 major steps of thermal degradation at 304 - 489°C and 493 – 551 °C for ENR/ZrO$_2$ composite at 50 mg ZrO$_2$ loading and 306 - 497°C and 512 – 581 °C for ENR/ZrO$_2$ composite at 100 mg ZrO$_2$ loading [13,14].

The increasing of temperature over weight loss percentage of the composites, particularly with high ZrO$_2$ loading indicate that the thermal stability has improved as ZrO$_2$ loading increased [15-17]. The char residue of ENR/ZrO$_2$ composites indicates the high molecular mass of Zr compared with purified ENR-25.

![Figure 4. TG thermogram of purified ENR-25 and ENR-25/ZrO$_2$ composites at 50 and 100 mg ZrO$_2$ loading.](image)

4. Conclusion

Based on FTIR spectra figure, the addition of ZrO$_2$ into ENR-25 formed bonds between Zr and epoxy unites. This type of bonding has improved the thermal stability of ENR/ZrO$_2$ samples as shown in TG thermogram.

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6. References

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