Influence of the synthesis parameters on the properties of natural rubber grafted poly-3-hydroxybutyrate

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Abstract. Graft copolymers of natural rubber (NR) and poly-3-hydroxybutyrate (PHB) with 60:40 ratio were synthesized in chlorobenzene. Two types of initiators namely azaoisobutyronitrile (AIBN) and benzoyl peroxide (BPO) AIBN and BPO were employed to initiate the free radical grafting of the two polymers. The influence of the various types of initiator loadings was also investigated. Estimation of the grafted NR was performed using FTIR. The thermal stability and crystallization behavior of NR-g-PHB was studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) TGA as well as DSC respectively. The absence of the C=C peak of NR in the FTIR spectra confirmed that PHB grafted on this site after the breakage of the C=C bond. The increase in initiator loading, improved the smoothness of the NR-g-PHB. Moreover, single Tg were observed for NR-g-PHB which indicate that no phase separation occurs and the thermal stability of pristine NR after grafting was improved compared with that of NR alone.

1. Introduction

The realization of the effect of synthetic polymers to environmental problems has gained momentum to the development of materials based on renewable resources. Polymers derived from biomass such as poly(3-hydroxybutyrate) (PHB) have received considerable attention nowadays. Polyhydroxybutyrate (PHB) is a natural occurring polymer produced by the microorganism, known as Bacillus megaterium and was discovered by Lemoigne in 1926 [1]. PHB is a semi-crystalline thermoplastic which is biocompostable, biocompatible as well as renewable in nature [2]. Because of these properties, PHB has been applied in applications such as in the biomedical field. PHB not only acts as a vehicle to transport nutrient, drug and bioactive molecule to the tissue or cell, but it also employed in tissue scaffolding for bone and nerve regeneration, cardiovascular as well as cartilage support respectively [3, 4]. Apart from this, PHB is also prominent in water treatment field. Heitmann and coworkers, demonstrated the degradation of methylene blue using PHB as a support to disperse nanostructured niobium oxyhydroxide [5].

While PHB has shown excellent properties, it is actually a very brittle plastic and prone to thermal degradation at temperatures above the melting point [6]. To a certain extent, this limits its application. In an effort to extend its use, various methods have been devised to improve the properties of PHB.
Chemical modification of PHB via grafting with natural rubber is an alternative method to incorporate desirable properties without sacrificing its biodegradable nature. Natural rubber is a good candidate as it is high elasticity and good rebound resilience [7]. Thus NR will act as a soft fragment to form a chemical linkage with the hard fragment of PHB to achieve better properties or processability. In addition, grafted NR with semi-crystalline PHB can improve the properties in terms of elasticity and brittleness of the original polymer. Studies have shown that PHB can be blended with other polymers such as ethylene propylene rubber [8], poly methyl methacrylates (PMMA) [9], polyethylene oxide [10] and poly-caprolactone (PCL) [11] respectively. However, most of the works report that the polymers do not mix well and a miscible system rarely occurs. For example, Graco and coworker studied the blending of PHB-ethylene propylene (EPR) system [12]. They concluded that no interactions occur between PHB and EPR after two distinct T_g values were observed. Hence, interests in PHB based blends have gradually shifted to reactive systems which allow better mixing and yet with only a simple preparation method. In the present study, natural rubber was selected to be grafted onto the PHB chains. This study describes graft polymerization of NR onto PHB by solution polymerization method using different types of initiator. Various parameters that affect the graft process were also investigated.

2. Materials
Natural rubber latex (NRL) with 60% dry rubber content (DRC) was obtained from Malaysian Rubber Board, Kuala Lumpur. Poly (3-hydroxybutyrate) was purchased from BIOCYCLE (Brazil) and purified before use [13]. The purification procedures are described in the following section 2. Chlorobenzene (99.7%) and acetone were purchased from Sigma Aldrich. Azoisobutyronitrile and benzoyl peroxide were manufactured by Fluka.

2.1. Preparation of dry rubber (DR)
Natural rubber latex (NRL) is used for the preparation of DR. NRL was dropped into a glass bottle containing acetone at room temperature. The acetone was removed after a while and the coagulants were washed again using acetone several times. Finally, the DR was dried in a vacuum oven at 40°C for 5 h or until constant weight was reached.

2.2. Preparation of natural rubber grafted poly(3-hydroxybutyrate) (NR-g-PHB) copolymer
NR/PHB with a 60:40 wt/wt ratio was dissolved in chlorobenzene at 105°C overnight. The initiator was added into the cooled polymer mixture at 30°C followed by 15 min stirring. The polymer mixture was cast in a glass mold, purged with argon gas, and covered with a glass plate. Afterwards, the NR-g-PHB was kept in the oven for 2 days at a certain casting temperature to maximize the grafting and cross-linking reactions. Then the glass plate was removed to achieve solvent evaporation at 105°C. Different parameters were investigated according to table 1.

| Table 1. Parameters study of NR-g-PHB. |
|--------------------------------------|
| **NR-g-PHB** | **Type of initiator** | **Casting Temperature (°C)** | **Initiator loading (% mole)** |
| 60:40 | AIBN | 90 | 7 |
| | BPO | 90 | 7 |
| 60:40 | BPO | 105 | 3 |
| | BPO | 105 | 5 |
| | BPO | 105 | 7 |
| | BPO | 105 | 10 |
2.3. Characterization

The possible structural changes of the samples were determined by Fourier Transform Infrared (FTIR) spectroscopy. The samples were scanned from 400-4000 cm⁻¹ using a Frontier Universal ATR Perkin Elmer FT-NIR Spectrometer. The thermal properties of the samples were studied using a Mettler Toledo Differential Scanning Calorimetry (Switzerland). As much as 10.00 mg of the samples was weighed in an aluminum pan covered with aluminum lid. The sample was heated from -100 to 190°C and held for 2 minutes at a heating rate of 20°C min⁻¹ under nitrogen environment. Next, the samples were quenched to -100°C at a scanning rate of 20°C min⁻¹ and held for another 2 minutes. Finally, the samples were again heated to 190°C at a heating rate of 20°C min⁻¹. The thermal stability of the as prepared samples were examined using a Perkin Elmer STA 6000 simultaneous thermal analyzer. As much as 5.00 mg of sample was heated from 30°C to 900°C at a heating rate of 20°C min⁻¹ under nitrogen flow.

3. Result and Discussion

3.1. Effect of initiator

Two initiators, which are azoisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were studied using 7% mol at 90°C, to investigate their effectiveness in grafting NR/PHB. When AIBN initiator was employed, breakages in the NR-g-PHB membranes were observed as compared to the BPO initiator, which gives a smoother NR-g-PHB surface as shown in figure 1(a-b). The breakage in NR-g-PHB membrane could be due to the insufficient occurrence of grafting and/or crosslinking between NR/PHB which can be proven by the dissolution of NR-g-PHB in chloroform solvent. AIBN is not an effective initiator for this purpose, mainly because of the resonance stabilization effect of radical (I) that changes to radical (II) as shown in figure 2(a). The formation of radical (II) reduces its reactivity and efficiency in generating active sites on the backbone of NR and PHB [14]. Thus, the reactivity of the initiator must be high enough in order to abstract allylic hydrogen from NR and PHB. Generally, based on previous work, grafting and crosslinking reaction for NR takes place at high temperatures [15, 16]. However, AIBN has shorter half-life in chlorobenzene at high temperature. Hence, the possibility of doing so using this initiator may not be advantageous due to the fact that fast decomposition of the AIBN radicals occurs at temperatures above 70°C. In contrast, BPO contains a weak sigma bond (O-O bond). Hence, it can rapidly undergo bond homolysis at or below 110°C to generate a pair of radicals as depicted in figure 2(b). These radicals are capable in abstracting a hydrogen atom from a carbon-hydrogen bond in either nature or PHB [17]. In addition, it can also be used at high temperatures due to the fact that the half-life of BPO in chlorobenzene is longer in comparison to AIBN. This can give enough energy for crosslinking and graft copolymerization to occur. Hence, in the rest of the study, BPO was used as the initiator in the preparation of NR-g-PHB system.

The effect of initiator loadings on the preparation of NR-g-PHB was investigated. The experiments were performed using various BPO initiator concentration ranging from 3 to 10% mol. Ratio of 60:40 of NR/PHB and a reaction temperature of 105°C were used. When the initiator loadings were increased from 3 to 7% mol, a homogeneous membrane was obtained. The increase in BPO loading can enhance the chance of hydrogen abstraction from the NR backbone. More free radicals produced from the dissociation of BPO resulting in more active sites on the NR and PHB backbones, thus facilitating grafting reaction. However, when the initiator loadings were continuously increased to 10% mol, small holes with little breakage was observed. This phenomenon may be explained as due to the excess initiator which can cause the free radical species to recombine and be involved in a termination reaction. Therefore, from those results, the optimum BPO amount is taken to be 7% mol.
Figure 1. Images of membranes obtained for different initiator (a) AIBN and (b) BPO using 7% mole at 90°C.

Figure 2. Radical formation from (a) AIBN and (b) BPO.

3.2. Characterization of NR-g-PHB
Figure 3 show FTIR spectra of pristine NR and PHB. NR shows several peaks as shown in figure 3 (a). The spectrum of NR confirms the availability of the C=C bond at 1661 cm$^{-1}$, while the 833 cm$^{-1}$ peak refers to the =C-H out of plane bending. Moreover, there are three peaks in the 2961 to 2852 cm$^{-1}$ region attributed to the asymmetry -CH$_3$, asymmetry and symmetry -CH$_2$- as well as -CH$_3$ correspondingly. On the other hand, the peaks at 1375 cm$^{-1}$ and 1446 cm$^{-1}$ represent the CH$_2$ and CH$_3$ bending of NR. In contrast, figure 3(b) shows the FTIR spectrum of PHB. The most important characteristic peak in the PHB spectra is the carbonyl stretching vibration (–C=O) which occurs at 1720 cm$^{-1}$. The –CH asymmetric and symmetric stretching show peaks at 2932 cm$^{-1}$ as well as 2974 cm$^{-1}$ respectively. In addition, the various modes of the CH$_3$ peak occurs at 1453 (asymmetric deformation), 1379 (symmetric deformation) and 826 cm$^{-1}$ (CH$_3$ bending). The intensity and frequency of all the peaks are very sensitive to structural changes.

Subsequently, figure 4 shows the NR-g-PHB spectrum prepared using various BPO loadings. As can be observed in figure 4, both characteristic peaks of PHB and NR were observed in the NR-g-PHB
spectra. As an example, the peak for asymmetry -CH$_3$, asymmetry and symmetry -CH$_2$- as well as -CH$_3$ of NR is found at 2966, 2932 and 2856 cm$^{-1}$ for 3, 5, 7 and 10% mol. Besides, the peak for C=O of PHB in 3, 5, 7 and 10% mol of initiator is observed at 1719 cm$^{-1}$. However, the peak of C=C of NR at 1661 cm$^{-1}$ is not found in the NR-g-PHB for all the spectra. This may be due to the C=C breakage which causes radical formation at that site. This is in a good agreement with Pongsathit and Pattamaprom [18], who discovered that there are two possible sites for free radical formation in NR. Free radical formation can occur at the C=C or at the allylic carbon atoms respectively. Interestingly, the significant reduction in the peak position of the CH$_3$ bending of PHB occurred as well from 826 cm$^{-1}$ to 801 cm$^{-1}$ after the reaction. These imply that, the reaction of PHB with the C=C of NR, thus the grafting of NR on PHB was successful. Figure 5, show a reaction mechanism for NR-g-PHB.

The change in the crystalline phase of PHB can further support that graft polymerization occurred. The FTIR spectra of the NR-g-PHB show the crystalline peak of PHB at 980, 1230 as well as 1720 cm$^{-1}$ such in figure 4. Obviously, the peak intensity of crystalline PHB at 980 and 1230 cm$^{-1}$ for NR-g-PHB was reduced as compared to PHB alone. In addition, an intense and broad shoulder peak at 1740 cm$^{-1}$ attributed to the amorphous region of PHB was observed for NR-g-PHB as shown in figure 6. The entanglement of the grafted NR may have obstructed the melting of crystalline phase of PHB, resulting in more amorphous PHB. Wei et al. [6], discovered a similar observation when grafting PHB onto cellulose causing a reduction in the intensity of the crystalline peak and high intensity of the amorphous PHB peak. Thus, it can be deduced that from FTIR result, the NR has been successfully grafted onto PHB.

**Figure 3.** FTIR spectra of (a) pristine NR and (b) purified PHB.
**Figure 4.** FTIR spectra of (a) 3% (b) 5% (c) 7% and (d) 10% mol of BPO initiator on NR grafting by PHB at 105°C.

**Figure 5.** Reaction mechanism of NR-g-PHB.
Figure 6. Expanded region FTIR spectra for PHB and NR-g-PHB with various initiator loading.

3.3. Thermogravimetry Analysis (TG-DTG)

TG and DTG thermograms of pristine NR, PHB and NR-g-PHB prepared with different % mol of BPO initiator are presented in figure 5. The values of degradation temperatures $T_1$, $T_2$ and $T_3$ as well as maximum degradation temperature ($T_{\text{max}}$) are summarized in table 2. As can be seen, NR and PHB exhibited single stage of thermal degradation profile, meanwhile a three stage thermal degradation profile was found for 3, 5 and 10% mol of NR-g-PHB. However, two stage thermal degradation profile was observed for 7% mol graft samples from room temperature to 900°C. Natural Rubber and PHB show that the $T_1$ occurs at 363°C and 286°C and $T_{\text{max}}$ values at 380°C and 292°C respectively. Meanwhile, for the NR-g-PHB, the first stage of degradation occurred at around 155-195°C with $T_{\text{max}}$ at 209-232°C is normally due to the short chain length of PHB. The second stage degradation at near 272-285°C with $T_{\text{max}_2}$ at 217-312°C is attributed to the grafted portion of PHB chains. The value of $T_2$ at the second stage is slightly lower as compared to $T_1$ of PHB. This is due to the heat transfer effect from the first stage triggered the $T_{\text{onset}}$ at the second stage to occur earlier. The third stage degradation temperature $T_3$ occurred in the temperature range 363-380°C with $T_{\text{max}}$ at 412-427°C was assigned to the degradation of cross-linked and graft NR. The maximum degradation temperatures of the graft polymer were higher than unmodified NR and PHB as shown clearly in the derivative thermogravimetric graph. This indicates that the NR-g-PHB has improved thermal stability compared to pristine PHB and NR. Furthermore, the amount of char residue of NR and PHB was not found whilst it was about 1-5% residual for the NR-g-PHB. In addition, grafting with 7% mol of initiator shows a higher residual around 5.13%. This result demonstrates the ability of NR-g-PHB to resist heat is higher in comparison NR and PHB alone.

| Different loading of BPO | $T_{\text{onset}}$ (TG curve) | $T_{\text{max}}$ (DTG curve) | Final Residual |
|--------------------------|-------------------------------|-----------------------------|----------------|
| NR                       | 363                           | -                           | 0              |
| PHB                      | 286                           | -                           | 0              |
| 3                        | 195                           | 272                         | 209            | 297 | 425 | 1.76 |
| 5                        | 198                           | 279                         | 364            | 215 | 290 | 425 | 3.28 |
| 7                        | -                             | 283                         | 363            | -    | 310 | 412 | 5.13 |
| 10                       | 155                           | 285                         | 380            | 232 | 312 | 427 | 1.88 |
3.4. Differential Scanning Calorimetry (DSC)

Figure 6 shows the DSC heating curves of NR and PHB as well as all the NR-g-PHB samples prepared from -100 to 190°C. The corresponding thermal data, including the glass transition temperature ($T_g$), melting temperature ($T_m$), crystallization temperature ($T_c$) and the calculated polymer’s crystallinity ($\chi_c$) are listed in table 3. Generally, the DSC curve in figure 6 shows only a single $T_g$ peak of PHB at 8.6°C. While the $T_m$ peak of the purified PHB occurred at 172.1°C respectively. Similar result was obtained in a previous report [19]. A single and distinct $T_g$ is observed in all NR-g-PHB samples. The $T_g$ for NR-g-PHB with 3, 5, 7 and 10% mol of BPO used are 0.56, -1.05, 2.90 and -0.45°C respectively. Herein, the appearance of single $T_g$ indicate no phase separation and confirm that grafting reaction has occurred. In addition, for 7% mol of BPO loadings show a higher $T_g$ probably due to the presence of the bulky grafted PHB on the NR molecule causes restriction on the chain mobility.

Two peaks of $T_m$ were observed in all the NR-g-PHB as shown in figure 6. The $T_m$ of all NR-g-PHB samples were slightly shifted to lower temperature as compared to purified PHB. For example, the $T_m$ peaks for PHB is 172°C, while for NR-g-PHB prepared with 3, 5, 7 and 10% mol are observed at 143-154, 141.3-153.4, 141.2-155.1 as well as 144.7-158.0 correspondingly. The double melting behavior may be explained by the dispersion of NR particles in PHB matrix that disturb the crystallization of PHB and leads to the formation of imperfect crystals. Xu et al revealed that the formation of the double $T_m$ peaks was attributed to the melting of the crystals formed during the non-isothermal crystallization of the first $T_m$ peak, whereas the second $T_m$ peak corresponds to the melting of the crystals formed through recrystallization and reorganization of the crystals of the first $T_m$ peak during the subsequent DSC heating scans [20]. Subsequently, a previous study mentioned that the shiftment to lower temperature possibly infers the presence of defects in the PHB crystals or lamellar structures in the NR-g-PHB [19].

On the other hand, the presence of NR may influence the crystallinity of PHB. Pristine PHB has no crystallization peak temperature ($T_c$). In the case of NR-g-PHB, $T_c$ shift to around 77.3, 87.5, 90.3 and 85.9°C, for the NR-g-PHB prepared using 3, 5, 7 and 10% mol respectively. It is obvious that $T_c$ of the NR-g-PHB are always higher, indicating that the presence of NR plays a role in accelerating the crystallization of PHB due to the nucleation effect in the graft polymer. Similar phenomenon is reported elsewhere [20]. The values for degree of crystallinity were lowered after grafting in comparison with the PHB from 55 to 1%. This trend corresponds to the PHB molecular chains aligned to form crystal structures which were hindered either by NR or by the slightly long chain branching of PHB homopolymer [6]. This is in a good agreement with an increased in the crystallization temperatures ($T_c$) of all grafted copolymers as compared to bulk PHB. A lower $X_c$ requires less energy to move the polymer chains in the amorphous phase, hence the crystallization of grafted copolymers from melts were initiated at higher temperature.

| Table 3. Thermal transition of NR, PHB and various NR/PHB blend. |
|---------------------------------------------------------------|
| **BPO Loadings** | $T_{g1}$ (°C) | $T_{m1}$ (°C) | $T_{m2}$ (°C) | $T_c$ (°C) | $X_c$   |
| NR             | -60.9        | -            | -            | -          | -       |
| 3              | 0.56         | 143.0        | 154.0        | 77.3       | 1.11    |
| 5              | -1.05        | 141.3        | 153.4        | 87.5       | 1.37    |
| 7              | 2.90         | 141.2        | 155.1        | 90.3       | 1.76    |
| 10             | -0.45        | 144.7        | 158.0        | 85.9       | 1.79    |
| PHB            | 8.6          | 172.1        | -            | -          | 55.0    |
4. Conclusion

In summary, this paper describes a study on amorphous/semi-crystalline graft system focusing on NR-g-PHB in terms of chemical interaction as well as thermal behavior. The use of BPO enables PHB to be grafted onto NR in a simple process. The properties of the NR-g-PHB materials could be tuned by varying reaction condition. The FTIR spectroscopic analysis indicated that, in the NR-g-PHB unveiled a grafting reaction occurred between them. This can be supported through DSC results. A single glass transition temperature was observed from DSC, which indicates no phase separation occurred. In addition, due to the new bonds formed via grafting the thermal stability of NR-g-PHB was improves as compared to pristine PHB and NR.

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