Raman spectra of polyethylene glycol/cellulose acetate butyrate biopolymer blend

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Abstract. In order to investigate their crystalline structure conformations, several ratio combinations of polyethylene glycol (PEG)/cellulose acetate butyrate (CAB) were studied by Raman spectroscopy. PEG/CAB spectral features due to the composition dependence revealed the gradual transformation from crystalline PEG-like structure to the amorphous CAB-like structure as increasing the ratio of CAB. Bands appeared in the C-H stretching area of 3000–2700 cm\(^{-1}\) and C-H bending area of 1500–1400 cm\(^{-1}\) clearly exposed the transition of the PEG to the CAB-spectral features with the transition point at about PEG/CAB (30/70). Band at 1737 cm\(^{-1}\) in the C=O stretching area of 1800–1650 cm\(^{-1}\) described the existence of a very weak hydrogen bond arise between PEG and CAB. In the C-O-C area of 1000–800 cm\(^{-1}\), drastic spectral change suggested that the hydrogen bond interaction takes place in the back bone of PEG.

1. Introduction
In the production of modern biopolymer materials, blending technique of natural polymers attracted significant attention. It is one of the most simple and inexpensive approaches for producing new polymer material with unique and attractive properties based on the characteristic of two or more polymers [1]. Polyethylene glycol was targeted in this study as it is one of the most commercially important polyether used for various applications [2]. Moreover, the development of the PEG polymer blend is still very popular. PEG has been successfully blended with several polymers such as poly (3-hydroxybutyrate) (PHB), poly (lactide) (PLA), poly(p-dioxanone) (PPDO), and poly(ε-caprolactone) (PCL) [3–6].

Cellulose acetate butyrate (CAB) is cellulose derivative that is suitable material to be combined with other polymers since it is readily abundant in the earth. CAB has been successfully blended with PHB producing a better mechanical toughness of PHB and improving PHB elongation of break [6–9]. However, there is a few studies have been reported on the blending of PEG and CAB.
Figure 1. Chemical structure of (a) Polyethylene Glycol (PEG) and (b) Cellulose Acetate Butyrate (CAB).

Figure 1 describes the chemical structure of PEG and CAB. In order to generate a good polymer blend system, hydrogen bond between these two polymers plays a prominent role in stabilizing the crystalline structure conformation of blend polymer system. The existence and role of this prominent hydrogen bond has been reported in numerous study in homo polymer [9–11], copolymer [12–14], and polymer blend system [15–18]. Therefore, this study has been focused on the monitoring of the hydrogen bond between PEG and CAB in order to understand crystalline structure conformation of PEG/CAB biopolymer blend.

2. Methods
Film sample of PEG/CAB biopolymer blend with multiple ratio combinations of (100/0), (90/10), (80/20), (70/30), (60/40), (50/50), (40/60), (30/70), (20/80), (10/100), and (0/100) were prepared by mixing low molecular weight of PEG (Mn = 2.0x10^4) and CAB (Mn = 6.5x10^4) obtained from Aldrich Chemical Co., Ltd. Without any purification process, PEG and CAB with determined weight were dissolved separately in chloroform (CHCl_3) at 60°C while stirring them until both of them completely solubilized. Blended the two solutions in a beaker glass and continue stirring for 48 hours at 60°C, the mixture was then transferred into a petri dish to evaporate the solvent at room temperature for 24 hours until a film sample was obtained. The thickness of the obtained film sample was controlled about 100μm thick by melted and pressed the sample on a hot plate. Finally, in order to achieve the perfect crystallization of the blend sample conformation, the 100μm thick film sample was inserted into a oven with a vacuum condition at 60°C for 12 hours. Raman spectra measurements have been done for the eleventh ratio combinations of the PEG/CAB film sample at room temperature. The measurements were conducted by using Kaiser Hololab 5000 with excitation wavelength of 785 nm, 4 cm^-1 number of resolutions, 10 times of accumulation number, and 10 second of exposure time.

3. Results and discussion
In Figure 2, Raman spectra of PEG/CAB biopolymer blend film sample with various ratio combinations of (100/0), (90/10), (80/20), (70/30), (60/40), (50/50), (40/60), (30/70), (20/80), (10/100), and (0/100) are seen in the C–H stretching area and C=O stretching area. In the C–H stretching area which lies from about 3000–2700 cm^-1 there are several bands can be obtained due to the presence of PEG and CAB. The highest PEG component of (100/0) have 6 bands appeared at 2946, 2937, 2911, 2886, 2836, and 2779 cm^-1. The crystalline stage of PEG is related to these bands. While, the highest CAB component of (0/100) shows 2 major bands at 2937 and 2875 cm^-1 also another 2 shoulder bands at 2965 and 2913 cm^-1 aligned to the amorphous stage of CAB. The additions of the CAB ratio in the PEG/CAB blend sample cause a change in the Raman spectra which is gradually transfer from the PEG-like spectrum to the CAB-like spectrum with transition point at the ratio combination of (30/70). It indicates that the crystalline conformation of the blend sample could be modified from the crystalline stage of PEG to the amorphous stage of CAB vice versa due to its ratio combination.
Figure 2. Raman spectra of PEG/CAB biopolymer blend film sample with eleventh ratio combinations measured at room temperature in the C-H stretching area (3000–2700 cm\(^{-1}\)) and C=O stretching area (1800–1650 cm\(^{-1}\)).

PEG does not have C=O functional group (Figure 1) hence there is no band of the highest ratio combination of PEG/CAB (100/0) appear in the area from about 1800–1700 cm\(^{-1}\) that has been known as C=O stretching area. On the other hand, PEG/CAB (0/100) shows a peak at 1737 cm\(^{-1}\) assigned to the C=O functional group of CAB amorphous stage (Figure 2). In the PEG/CAB ratio combinations of (80/20), (70/30), (60/40), (50/50), (40/60), (30/70), (20/80), and (10/90), this C=O stretching band is clearly appeared. On the case of PEG/CAB (90/10), the baseline at around 1737 cm\(^{-1}\) slightly increases with small number of signals to noise ratio. Therefore, it is difficult to determine whether that is a real peak or not. As the inclusion of PEG ratio in the blend samples, the peak position of this C=O stretching band is somewhat moved to the lowest wavenumber. This phenomenon indicates that there might be an interaction occurs between PEG and CAB which most likely a hydrogen bond interaction. This interaction has a prominent role in stabilizing PEG/CAB biopolymer blend structure. The band position at around 1737 cm\(^{-1}\) is little bit higher than the C=O stretching band of poly(3-hydroxybutyrate) (PHB) at 1723 cm\(^{-1}\) associated with a weak hydrogen bond interaction [19]. Therefore, the little higher position of PEG/CAB C=O stretching band indicates that PEG-CAB possess a weaker hydrogen bond interaction compare than a homopolymer PHB.

Figure 3 presents Raman spectra of PEG/CAB biopolymer blend film sample with various ratio combinations of (100/0), (90/10), (80/20), (70/30), (60/40), (50/50), (40/60), (30/70), (20/80), (10/100), and (0/100) in the C-H bending area and C-O-C stretching area at around 1500–1400 cm\(^{-1}\) and 1000–800 cm\(^{-1}\) respectively. In the C-H bending area pure PEG (100/0) shows 3 bands at around 1480, 1467, and 1445 cm\(^{-1}\) due to the crystalline phase of PEG. On the other hand pure CAB (0/100) has 2 bands appear at around 1451 and 1415 cm\(^{-1}\) due to the amorphous phase of CAB. The blend of PEG and CAB with increases PEG ratio resulting in a change of the form of spectra; from the PEG-like spectra to the CAB-like spectra with the transition point at around (30/70). It is a same result with the spectra behavior of the blend sample in the C-H stretching area. Therefore, because of the blending ratio modification, it also reveals that the crystalline structure conformation of PEG turns into the amorphous structure conformation of CAB.
Figure 3. Raman spectra of PEG/CAB biopolymer blend film sample with eleventh ratio combinations measured at room temperature in the C-H bending area (1500–1400 cm⁻¹) and C-O-C stretching area (1000–800 cm⁻¹).

Spectral bands obtained in the C-O-C stretching area of Raman spectroscopy represent back bone of polymers. In this C-O-C stretching area, there are 2 major bands of the pure PEG at around 859 and 843 cm⁻¹ related to the crystalline structure conformation of PEG. While, pure CAB shows bands at 923, 895, 866, and 836 cm⁻¹ due to its amorphous structure conformation. The change of PEG-like spectra to CAB-like spectra also can be seen in this area clearly with the same transition point at around PEG/CAB (30/70). Among the entire spectra area, the spectra transformations in this area are very obvious. It is the indication that in the PEG back bone, the hydrogen bond between two polymers PEG and CAB mostly occurs.

4. Conclusion
Crystalline structure transformation of PEG/CAB biopolymer blend has been investigated in this study by using Raman spectroscopy. There are 4 areas in Raman spectra; C-H stretching area (3000–2700 cm⁻¹), C=O stretching area (1800–1700 cm⁻¹), C-H bending area (1500–1400 cm⁻¹), and C-O-C stretching area (1000–800 cm⁻¹) that provided the information of the spectra transformation from the PEG-like structure to the CAB-like structure along with the addition of CAB ratio in the blend composition. Spectra features in the C-H stretching and C-H bending areas clearly exposed the transition point at about PEG/CAB (30/70). In the C=O stretching area, the band at 1737 cm⁻¹ defines the hydrogen bond that could exist between PEG and CAB, which is weaker than a PHB homopolymer. Moreover, the dramatic shift in the C-O-C area of the spectra revealed that the hydrogen bond occurs mainly in the back bone of PEG.

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