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Research Article

Effect of immobilization methods on the production of polyethylene-cellulose biocomposites via ethylene polymerization with metallocene/MAO catalyst

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Abstract

Polyethylene-cellulose biocomposites were synthesized here via the ethylene polymerization with metallocene as a catalyst along with methylaluminoxane (MAO) as a cocatalyst. The immobilization method in which the catalyst or cocatalyst is fixed onto the catalytic filler (cellulose) can be classified into 3 methods according to the active components fixed onto the filler surface: 1) only metallocene catalyst (Cellulose/Zr), 2) only MAO cocatalyst (Cellulose/MAO) and 3) mixture of metallocene and MAO (Cellulose/(Zr+MAO)). It was found that the different immobilization methods or different fillers altered the properties of the obtained composites and also the catalytic activity of the polymerization systems. It was found that Cellulose/MAO provided the highest catalytic activity among all fillers due to a crown-alumoxane complex, which caused the heterogeneous system with this filler behaved similarly to the homogeneous system. The different fillers also produced the biocomposites with some different properties such as crystallinity which Cellulose/Zr provided the highest crystallinity compared with other fillers as observed by a thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC). Nevertheless, the main crystal structure indicated to the typical polyethylene was still observed for all obtained biocomposites with different fillers as observed by an X-ray diffractometer (XRD).

Keywords: Polyethylene; Metallocene; Cellulose; Biocomposite

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1. Introduction

Polyethylene (PE) is the most widely used plastic in this world [1]. Its applications include packaging, construction, electrical, automotive, medical devices, toys, tubes, films, and so on. This is due to its interesting properties such as toughness, durability, excellent chemical resistance, and light-weight. It is a member of the polyolefin family, and can be classified into three main types: linear low-density

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polyethylene (LLDPE), low density polyethylene (LDPE), and high density polyethylene (HDPE) depending on its branching and density [2]. Nowadays, use of polyethylene is seriously concerned as its non-biodegradability causes severe environmental impacts. To reduce those impacts, some natural biodegradable fillers are added into polyethylene to enhance its biodegradability to some extent. The fillers used for this purpose include banana stem fiber [3], grass fiber [4], palm leaf [5], guayule biomass [6], and coconut shell powder [7]. However, the difference of polarities between polyethylene and natural fillers leads to the filler agglomeration in the obtained biocomposite, and thus the desired properties could not be attained. An *in situ* polymerization in which the fillers are introduced during the polymerization has proven to be the process that produces the biocomposites with good distribution of the fillers throughout the polymer matrices as seen in our previous works [8,9]. In those works, the *in situ* polymerization with a metallocene catalyst and MAO as a cocatalyst was conducted by immobilizing the MAO onto the filler surface and then being introduced into the polymerization systems along with the liquid metallocene. Nevertheless, for the in situ polymerization systems, metallocene and also a mixture of metallocene and MAO can be immobilized onto the filler prior the polymerization as well [10]. The difference in those immobilization methods can alter the catalytic performance of the system, and the properties of the obtained composites. Hlatky [10] classified the immobilization methods into 3 routes, i.e. route A: the MAO is first immobilized onto the filler and then the metallocene, route B: the mixture of metallocene and MAO is immobilized onto the filler, and route C: the metallocene is first immobilized onto the filler and then the MAO. It was described that route C is not attractive due to the steric effect between the complex structure of the metallocene and the filler surface. However, route C provides the covalent bonds between the metallocene and the fillers which can prevent leaching of polymer from the fillers into liquid phase, and then enhance the morphology control. Thus, all 3 routes are still developed by many authors in the recent years [11−15]. It should be noted that for route A and C the second component to be immobilized whether metallocene or MAO may be simultaneously immobilized during the polymerization for some studies.

In our previous study, microcrystalline cellulose (MCC) was used as a biodegradable filler compared with synthesized bacterial celluloses for producing of polyethylene/cellulose biocomposites using route A immobilization [8]. It was found that MCC provided the highest catalytic activity among other celluloses. The obtained biocomposites with MCC also exhibited good distribution of the filler with no XRD peaks of MCC observed in the biocomposites (suggesting no agglomeration of MCC formed inside the biocomposite). In fact, besides its biodegradability which may exert into its biocomposite, the MCC also showed a strong influence on the mechanical properties improving the elongation at break, fracture stress, and ultimate strength of the obtained composites as observed by Mubarak and Abdulsamad [16] in preparation of LDPE blended with MCC.

Therefore, in this study MCC was then further investigated using the *in situ* ethylene polymerization with various immobilization methods to observe changes in its catalytic performance. The immobilization of cocatalyst (MAO) or metallocene catalyst onto the cellulose were performed with three different methods including (A) immobilized metallocene catalyst on the cellulose (Cellulose/Zr), (B) immobilized MAO cocatalyst on the cellulose (Cellulose/MAO), and (C) immobilized the mixture of metallocene and MAO on the cellulose (Cellulose/(Zr+MAO)). The obtained PE/cellulose biocomposites were characterized by different techniques including scanning electron microscopy (SEM), thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC) and X-ray diffraction (XRD). The finished immobilized fillers were also investigated with energy dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectroscopy (FT-IR) to determine the different characteristics of the filler prepared from various immobilization methods. The catalytic activity of the polymerization systems in the presence of different fillers, and the biocomposite properties were discussed in detail.

2. Materials and Methods

The metallocene catalytic systems are always prepared and handled under an inert atmosphere due to the metallocene being a pyrophoric material [17]. Therefore, moisture and oxygen should be avoid in the system. In this research, Schlenk line, including vacuum line and nitrogen gas line with several stopcocks, and Glove box (MRBAUN LABstar) were used to control and eliminate moisture and oxygen.

2.1 Materials

rac-Ethylenebis(indenyl)zirconium dichloride or zirconocene ([Et(Ind)$_2$ZrCl$_2$]) as a metallocene catalyst was supplied from Sigma-Aldrich, Thailand. Methylaluminoxane (MAO) was supplied by Tosoh Finechem, Co., Ltd., Japan. Ethylene gas (99.99%) was donated by National Petrochemical Co. Ltd., Thailand. Microcrystalline cellulose (Avicel PH 101) was supplied from FMC Chemical (Thailand) Ltd., Thailand. Toluene was purchased from S.M.Chemical Supplies Co., Ltd. TEA was donated by Thai polyethylene Co., Ltd. Hydrochloric acid (HCl) (fuming 36.7%) was purchased from Aldrich chemical company, Thailand. Methanol (commercial grade) was supplied from SR lab, Thailand.

2.2 Preparation of Fillers

2.2.1 Calcination

Commercial cellulose (Avicel PH101) was calcined under vacuum at 150 °C with heating rate of 10 °C/min for 4 h. After that, the calcined cellulose was cooled down at room temperature and stored in bottle under inert atmosphere.

2.2.2 Immobilization

Three immobilization methods were used here for preparing the cellulose fillers as follows:

A. Immobilized only the metallocene catalyst (Et(Ind)$_2$ZrCl$_2$) on the cellulose; the obtained filler designated as "Cellulose/Zr".
B. Immobilized only the MAO cocatalyst on the cellulose; the obtained filler designated as "Cellulose/MAO".
C. Immobilized a mixture of metallocene and MAO on the cellulose; the obtained filler designated as "Cellulose/(Zr+MAO)".

The ratio of cellulose fillers and the immobilized materials in toluene was fixed at 1:10 (the proper ratio which the filler can be well dispersed in the solvent and the solvent can be removed in a short period). In addition, toluene is usually used as solvent for MAO because it is an aromatic solvent that do not cause any problem when dissolves the MAO, and therefore the commercial MAO is kept in the toluene solution [18]. The slurry mixtures were stirred at room temperature for 1 h, and then vacuum dried to obtain the solid powders designated as Cellulose/Zr for the filler prepared with method A, Cellulose/MAO for the filler prepared with method B, and Cellulose/(Zr+MAO) for the filler prepared with method C.

2.3 *In situ* Polymerization

The ethylene polymerization reactions were performed in a 100 mL semi-batch stainless steel autoclave reactor with magnetic stirrer. The 1.5 mL of Et(Ind)$_2$ZrCl$_2$ (5 x10^{-5} M) catalyst solution and MAO were added into reactor for the homogeneous catalytic system. For the heterogeneous catalytic systems, the certain amounts of fillers were added into the polymerization systems along with the metallocene or MAO solution to complete the systems. Nevertheless, all systems were controlled with the fixed molar ratio of $[Al]_{MAO}/[Zr]_{cat}$ at 2000 (when [Al] is referred to moles of Al from MAO and [Zr] is referred to mole of Zr from the metallocene catalyst) [19]. Toluene as a solvent was added into the reactor to make a total volume of 30 ml. The reactor was stirred and heated up to polymerization temperature (70 °C). Polymerization reactions were started when ethylene gas was fed under 3.5 bar into the reactor. The reactions were operated for 15 min, and then terminated by acidic methanol. The obtained polymer was filtrated and dried at room temperature [9,20].

2.4 Characterization

2.4.1 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The morphology of cellulose, cellulose fillers after immobilization, polymer and biocomposites were investigated using JEOL mode JSM-6400 model of SEM. The elemental distributions of elements on the materials were observed by EDX using Link Isis series 300 program.

2.4.2 Thermal gravimetric analysis-differential scanning calorimetry (TGA-DSC)

The melting temperatures (T_m) and crystallinity (X_c) of the samples were analyzed using TA Instruments SDTQ600 analyzer and DSC 204 F1 phoenix. The operation temperature ranged from 10 to 150 °C with a heating rate of 10 °C/min.

2.4.3 X-ray diffraction (XRD)

The bulk crystallinity of cellulose, cellulose fillers after immobilization, polymer and biocomposites was determined using a SIEMENS D-5000 X-ray diffractometer with CuK$_\alpha$ radiation (λ = 1.54439×10^{-10} m) and Ni filter. The spectrum was scanned in the 2θ range of 10 to 80 degrees with scan rate of 2.4 degree/min.

2.4.4 Fourier transforms infrared spectrophotometer (FTIR)

The functional groups of the cellulose and cellulose fillers were determined using Nicolet 6700 FTIR spectrometer with ATR mode. The small amount of samples was casted as thin film on NaCl plates under inert gas to prevent moisture and oxygen. The FTIR spectra were obtained with scanning range from 400-4000 cm^{-1} with 100 scans at resolution of 4 cm^{-1}.

3. Results and Discussion

3.1 Characterization of Cellulose and Filler

The morphology obtained from the SEM technique of the samples including the cellulose before immobilization, Cellulose/Zr, Cellulose/MAO, and Cellulose/(Zr+MAO) are shown in Figure 1. It was found that the pristine cellulose (Figure 1a) exhibited flake-like shape and smooth layer surface, looking similar to Cellulose/Zr. This suggests that the catalyst (metallocene) immobilized on the cellulose surface does not change morphology of the cellulose. The low amount of the metallocene used in the immobilization may not significantly affect the surface characteristic of the cellulose, and it also well distributed onto the cellulose surface thus being not observed by the SEM. For Cellulose/MAO and Cellulose/(Zr+MAO), they both exhibited a rough surface with the particles covering the cellulose. Those particles may be the MAO-agglomerated particles because immobilizing only metallocene did not change the morphology of the filler (Cellulose/Zr) as seen in the fillers immobilized in the presence of MAO. Nevertheless, Cellulose/(Zr+MAO) exhibited slightly smaller particles on the surface than Cellulose/MAO probably because the presence of the metallocene in the Cellulose/(Zr+MAO) may reduce the ag-

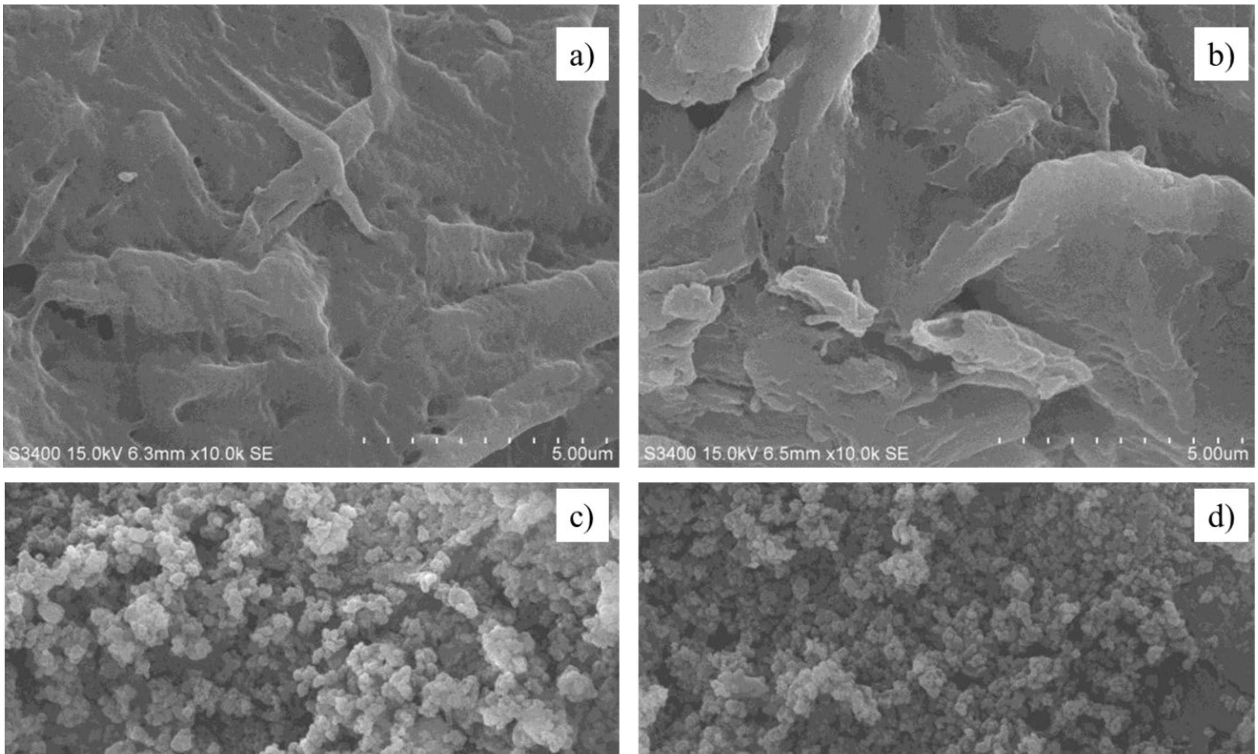

Figure 1. SEM micrographs of the samples: (a) Cellulose, (b) Cellulose/Zr, (c) Cellulose/MAO, and (d) Cellulose/(Zr+MAO).

glomeration of the MAO leading to the smaller particles. In addition, the morphology of Cellulose/MAO in this study was similar to the cellulose fillers (MCC) immobilized with MAO which had been observed in our previous study [8].

In order to investigate the distribution of the metallocene and the MAO onto the sample surfaces, the energy dispersive X-ray analysis (EDX) is used in conjunction with the SEM (SEM/EDX) was used. The SEM/EDX is an analytical technique used to provide the elemental identification and quantitative compositional information, and the distribution and intensity of the defined elements over the scanned area. The SEM/EDX images (Figure 2) provided the elemental mapping of the fillers which showed the location of elements (Zr and Al) as glowing dots over the scanned areas. In this place, Zr indicates to the metallocene [$Et(Ind)_2ZrCl_2$] on the filler, while Al indicates to the MAO [$(Al(CH_3)O)_n$]. From Figure 2, it was observed that for the fillers with only the metallocene (Cellulose/Zr) or the MAO (Cellulose/MAO), Zr and Al were both well distributed all over the fillers. Al exhibited higher density than Zr as expected due to the higher moles of MAO was introduced during the immobilization. When both metallocene and MAO were immobilized on the filler (Cellulose/(Zr+MAO)), Zr and Al still exhibited well distributed all over the filler suggesting that both metallocene and MAO could be simultaneously introduced into the immobilization process without diminishing their individual distribution.

The crystallinity of the cellulose and the fillers was investigated using an X-ray diffractrometer (XRD), and the XRD patterns of all samples were shown in Figure 3. It can

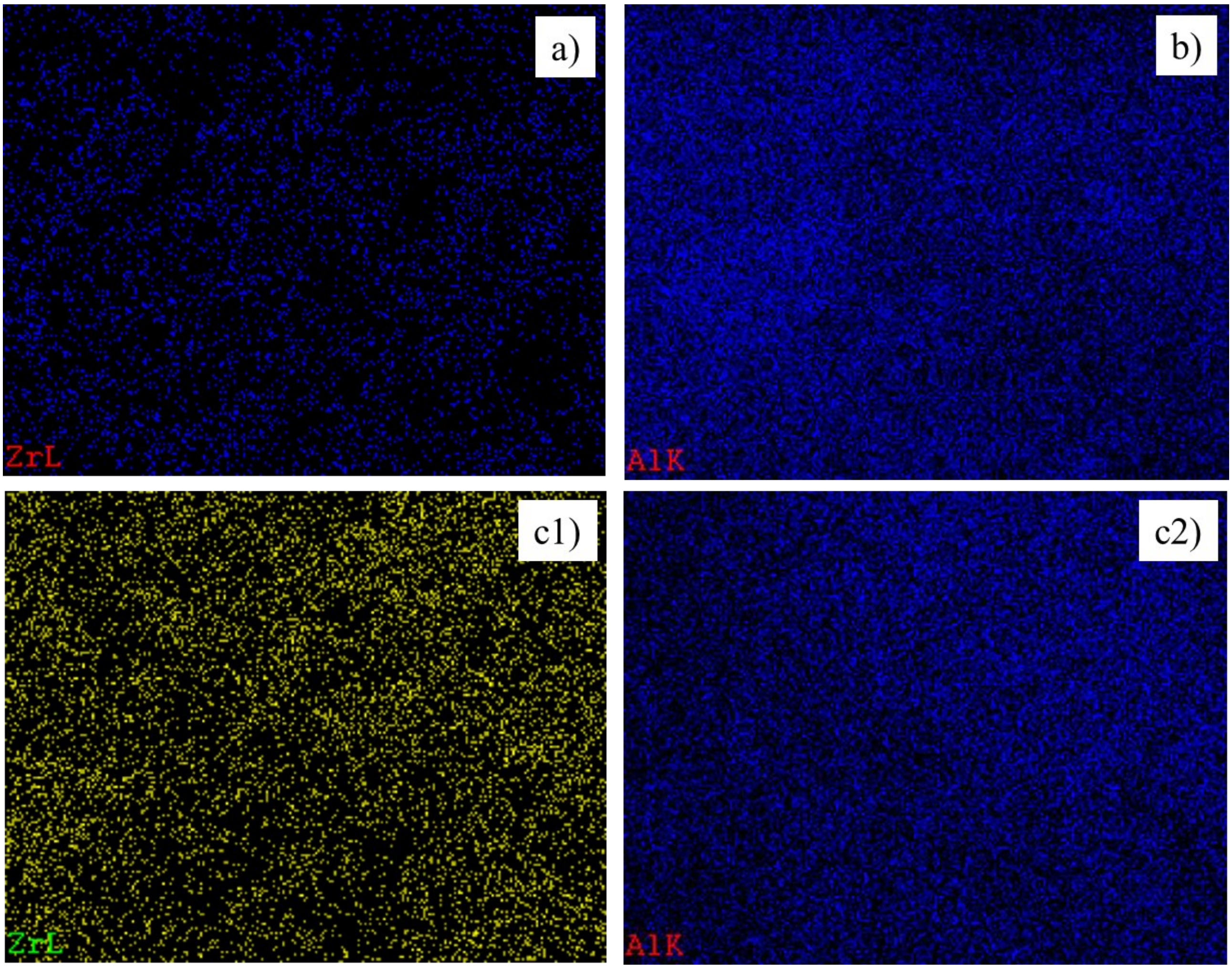

Figure 2. Elemental distribution obtained from SEM/EDX of various fillers. (a) Zr distribution of Cellulose/Zr, (b) Al distribution of Cellulose/MAO, and (c1) Al distribution and (c2) Zr distribution of Cellulose/(Zr+MAO).

be seen that the cellulose prior immobilization presented the characteristic peaks at 2θ equal to 14.8, 16.2, 22.5, and 34.5° corresponding to the cellulose sample with Miller indices (101) (002) (040) [21,22]. For the fillers immobilized with MAO (Cellulose/MAO and Cellulose/(Zr+MAO)), they presented broader peaks than the pristine cellulose due to the lower crystallinity resulted from the presence of MAO. The filler immobilized with only metallocene (Cellulose/Zr) slightly changed the crystallinity of the cellulose as seen that its XRD pattern was nearly the same as that of the cellulose. Nevertheless, there were no additional peaks observed in all fillers that could correspond to the metallocene or MAO. This indicates good distribution of both metallocene and MAO of the filler so they cannot be detected by the XRD measurement.

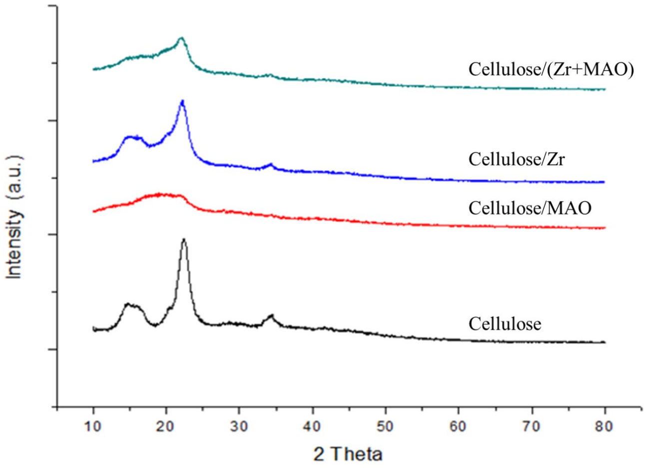

Figure 3. XRD patterns of cellulose and fillers.

The functional groups of all samples were characterized by Fourier transform infrared spectroscopy (FT-IR). In Figure 4, the FTIR spectra of the cellulose exhibited a broad band between 3000 and 3600 cm^{-1}, indicating to the stretching vibration of boned hydroxyl group on the cellulose. A peak at 2912 cm^{-1} was assigned to the C–H stretching vibrations in methyl and methylene groups. Peaks at 2160, 2024 and 1975 cm^{-1} appeared due to ATR-diamond crystal of FTIR instrument. Peaks at 1315 and 1427cm^{-1} were attributed to the asymmetric CH_2 bending vibration, while peaks at 1023 cm^{-1} corresponded to the C−O−C stretching of the β-1,4-glycosidic in cellulose [23]. For the spectra of the fillers, it obviously seen that broad peaks between 3000 and 3600 cm^{-1} (hydroxyl groups, −OH) all decreased compared with that of the cellulose. This suggests that the metallocene and MAO were linked with the cellulose through hydroxyl groups, thus those groups being reduced after immobilization. Most characteristic peaks of the cellulose were disappeared when immobilized with the metallocene (Cellulose/Zr and Cellulose/(Zr+MAO)). This is due to the complex structure of the metallocene probably

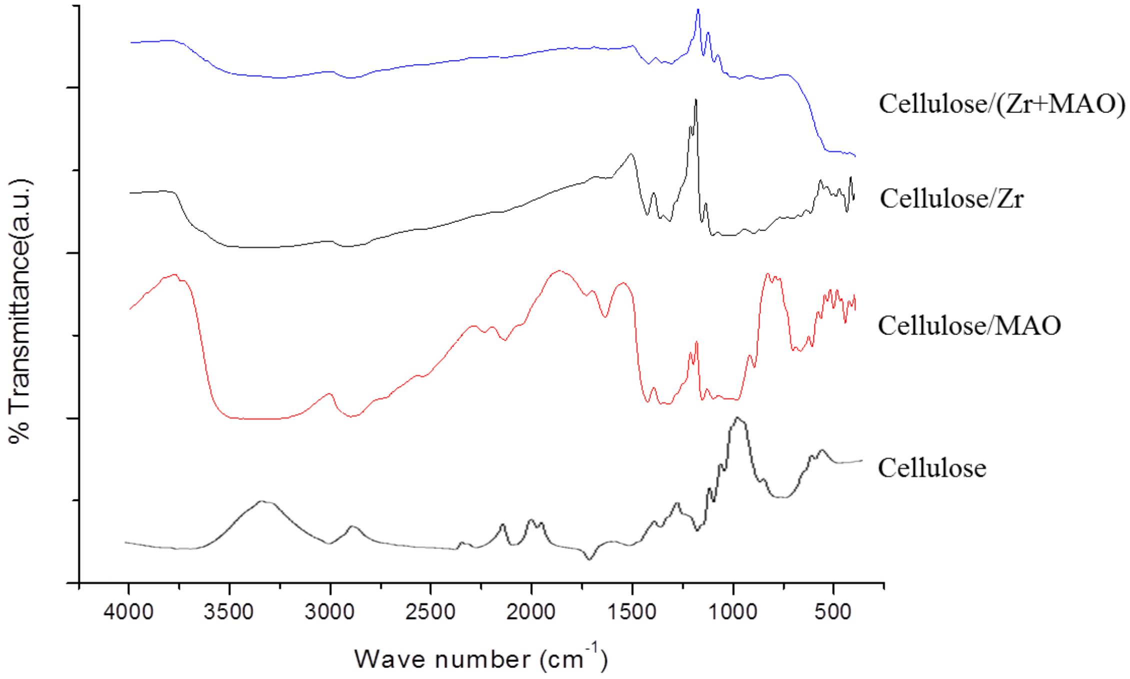

Figure 4. FT-IR spectra of cellulose and fillers.

providing complicated interaction with the cellulose.

3.2 Catalytic Activity

The fillers with the catalytic active species on them (metallocene or MAO) were then introduced into the polymerization systems known as the heterogeneous system. The catalytic activities of each system were detected based on the polymer yield obtained in the fixed-time period. In addition, the polymerization system without the fillers (homogeneous system) was also investigated. The catalytic activities of all systems were shown in Table 1.

It can be observed that the homogeneous systems without the solid fillers (run 1) provided the highest catalytic activity among other heterogeneous systems (run 2-4). This was due to the negative supporting effects arising from the presence of the solid fillers, no matter what types of the fillers are in the system. The fillers prevent the monomer access into the catalytically active sites, and generate strong interaction between the catalytically active sites and the filler surface, which reduce the reactivity of the catalysts toward the monomer [9,10,23]. However, most polyolefin industrial plants with metallocene catalysts are designed to use heterogeneous system in order to avoid major disadvantages of homogeneous catalysts such as reactor fouling and difficulty to control the morphology [24]. Therefore, the heterogeneous systems with the fillers are still essential and should be further developed.

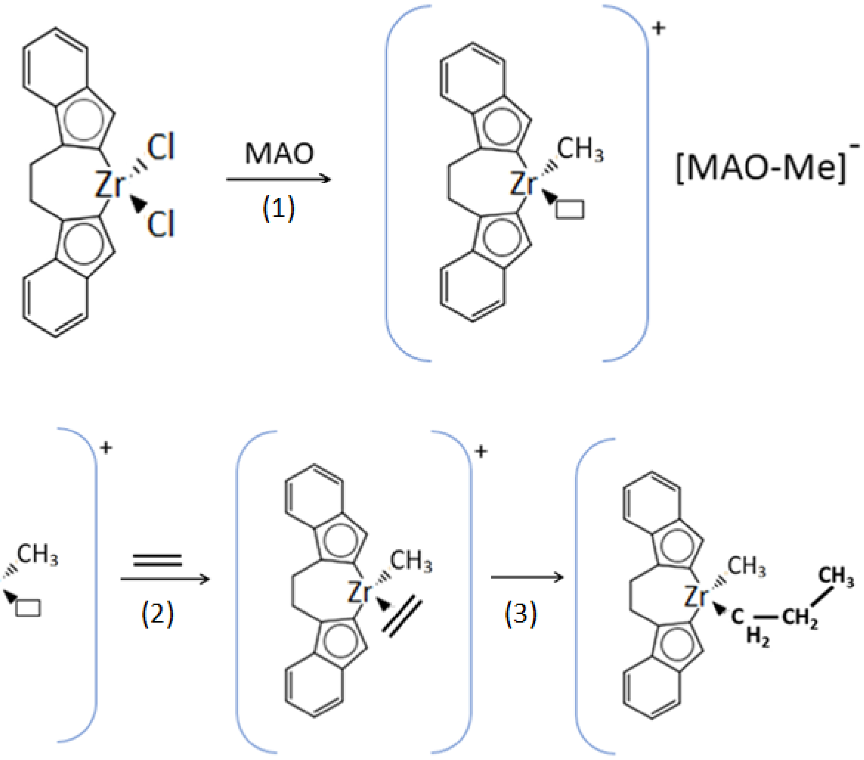

Figure 5. Mechanism of ethylene polymerization with metallocene catalyst [19,26-27].

Table 1. Polymer yield and activity of various polymerization systems, and polymer sample designation.

Run	Polymerization systems	Filler (g)	Polymer yield (g)	Catalytic activity ($kg_{PE}.\ g^{-1}_{Cat}.h^{-1}$)	Polymer samples
1	Homogeneous	-	0.6265	301.9	PE
2	Heterogeneous	Cellulose/Zr	0.1593	76.8	PE-Cellulose/Zr
3	Heterogeneous	Cellulose/MAO	0.1608	77.5	PE-Cellulose/MAO
4	Heterogeneous	Cellulose/(Zr+MAO)	0.1530	73.7	PE-Cellulose/(Zr+MAO)

Among the heterogeneous systems, run 3 in the presence of Cellulose/MAO showed the highest catalytic activity followed by run 2 and 4 in the presence of Cellulose/Zr and Cellulose/(Zr+MAO), respectively. In order to clarify this result, the mechanism of the polymerization with metallocene/MAO catalyst was reviewed here. This polymerization is classified as coordination polymerization, which the metallocene catalyzes the system with available cationic active sites (Zr^+) on it, where monomers attack and grow the polymer chain (step 2-3 in Figure 5). These cationic active sites are generated by being reacted with the MAO cocatalyst. After the reaction, the MAO turns into an anionic species acting as counterion for stabilizing the cationic active sites (step 1) [23]. It should be noted that the linkages between the filler and either metallocene or MAO are the covalent bond, while the linkages between metallocene and MAO are the ionic bond. Therefore, Cellulose/Zr and Cellulose/MAO had the active components firmly immobilized on them through the covalent bond. For Cellulose/(Zr+MAO), the active components are interacted with each other in solution forming the ionic bond prior linking with the fillers, and thus the ability of the active components to be immobilized onto the filler may be lower. The weak interaction between active components and filler surface of Cellulose/(Zr+MAO) likely causes the active components leaching from the filler surface during both immobilization and polymerization processes, leading to the lower catalytic activity. Nevertheless, there was a study showing that the system with immobilizing the mixture of metallocene and MAO onto the solid filler exhibited the higher catalytic activity than immobilizing only the metallocene onto the solid filler [25]. This is due to activating the metal component in solution creating more number of active centers than carrying out the process with one component in an immobilized state [10]. Therefore, it can be concluded that for this study, the effect of weak interaction between the active components and filler surface was more profound than that of generation more number of active centers.

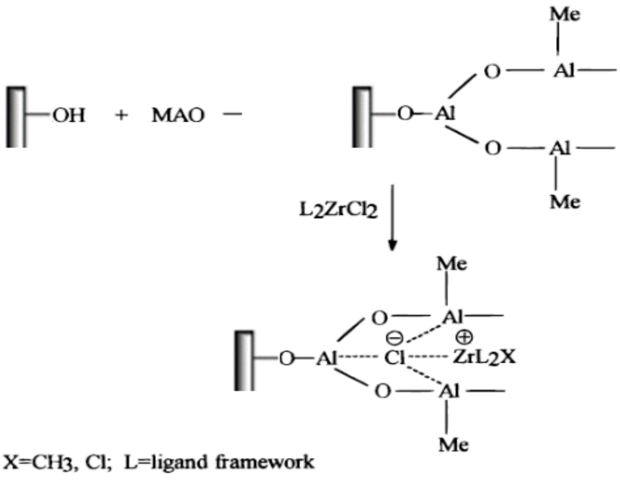

Figure 6. Formation of a "crown-alumoxane complex" by immobilization with MAO [29-30].

When comparing between Cellulose/Zr and Cellulose/MAO on which only one active component was immobilized, Cellulose/MAO exhibited the higher catalytic activity. This similar result has been described by Kaminsky and Renner [28] that a more homogeneous behavior when the MAO is immobilized first, and a closer interaction of the cationic center with the filler when the metallocene is immobilized first. The more homogeneous behavior of Cellulose/MAO is derived from the appearance of "crown" aluminoxane complexes as shown in Figure 6 [29−30]. The covering of MAO on the filler surface is postulated that the cationic zirconocene species floats over the solid surface, much like in solution. Therefore, it causes Cellulose/MAO to have high catalytic activity as occurring in the homogeneous system in run 1. For the closer interaction of the cationic center with the filler of Cellulose/Zr, it hinders Cellulose/Zr from the interaction with other components including the MAO and also the monomer, thus reducing the catalytic activity.

Although the mentioned study used silica as filler (support) [20], while this study used cellulose, both fillers had the same linkage group, i.e. hydroxyl groups. However, the different amount of the hydroxyl groups on both materials may be one of the crucial factors that influence their catalytic performance. In our previous work, which used silica as a filler immobilized with MAO, the catalytic activity of the heterogeneous system with this fillers decreased by 50% compared with the homogeneous systems [20]. However, in this study with the cellulose (Cellulose/MAO), it decreased by 75%. The higher amount of hydroxyl groups of cellulose (19 mmol/g, [31]) compared with silica (1.36 mmol/g, [32]) should be one of the main reason for the lower catalytic activity in cellulose. There also has been a study reporting that the hydroxyl groups have a deleterious effect on the catalyst [33].

3.3 Characterization of Polymer

Morphologies of all samples were obtained from a scanning electron microscope (SEM), and the SEM micrographs of the samples are shown in Figure 7. It can be seen that the polymer sample produced from the homogeneous system (polyethylene, PE) exhibited the agglomeration of fine particles. A matrix of polymer growth covering on the filler was observed in the polymers (biocomposite) obtained from the heterogeneous systems including PE-Cellulose/Zr, PE-Cellulose/MAO, and PE-Cellulose/(Zr+MAO). Producing polymers with less fine particles is the advantage of the heterogeneous system over the homogeneous system, which can reduce reactor fouling problem during ethylene polymerization and easily handle during polymerization processing [23]. Therefore, the cellulose reveals to be a natural material that can retain the benefit of solid fillers for the heterogeneous system, as many previously used fillers like silica, titania and alumina, etc. [20,34,35]. Nevertheless, the polymer from the heterogeneous system with immobilization of both metallocene and MAO onto the filler (PE-Cellulose/(Zr+MAO)) exhibited some characteristic of the one from the homogeneous system with the slight amount of the agglomeration of fine particles appearing on the surface. This is due to leaching of the active component into liquid phase derived from the weak interaction between active components and filler surface of Cellulose/(Zr+MAO) as mentioned above. Therefore, the effect of immobilization methods also exerted onto the morphology of the obtained polymers.

Crystal structures of all samples were characterized by an XRD technique as shown in Figure 8. It was observed that all XRD patterns were similar showing two sharp peaks of 2θ at 21.3° and 23.7°, which is assigned to the orthorhombic crystalline form in polyethylene [36]. This suggests that the obtained PE from the homogeneous system and PE-cellulose biocomposites exhibited the same crystal structure as typical polyethylene. In addition, no differences in crystal structure were observed among the biocomposites obtained from various immobilization methods. The characteristic peaks of the cellulose did not appear in the XRD patterns of all samples suggesting that the cellulose fillers inside were well distributed throughout the polymers, thus being not deflected by the X-ray.

The melting temperature (T_m) and crystal-

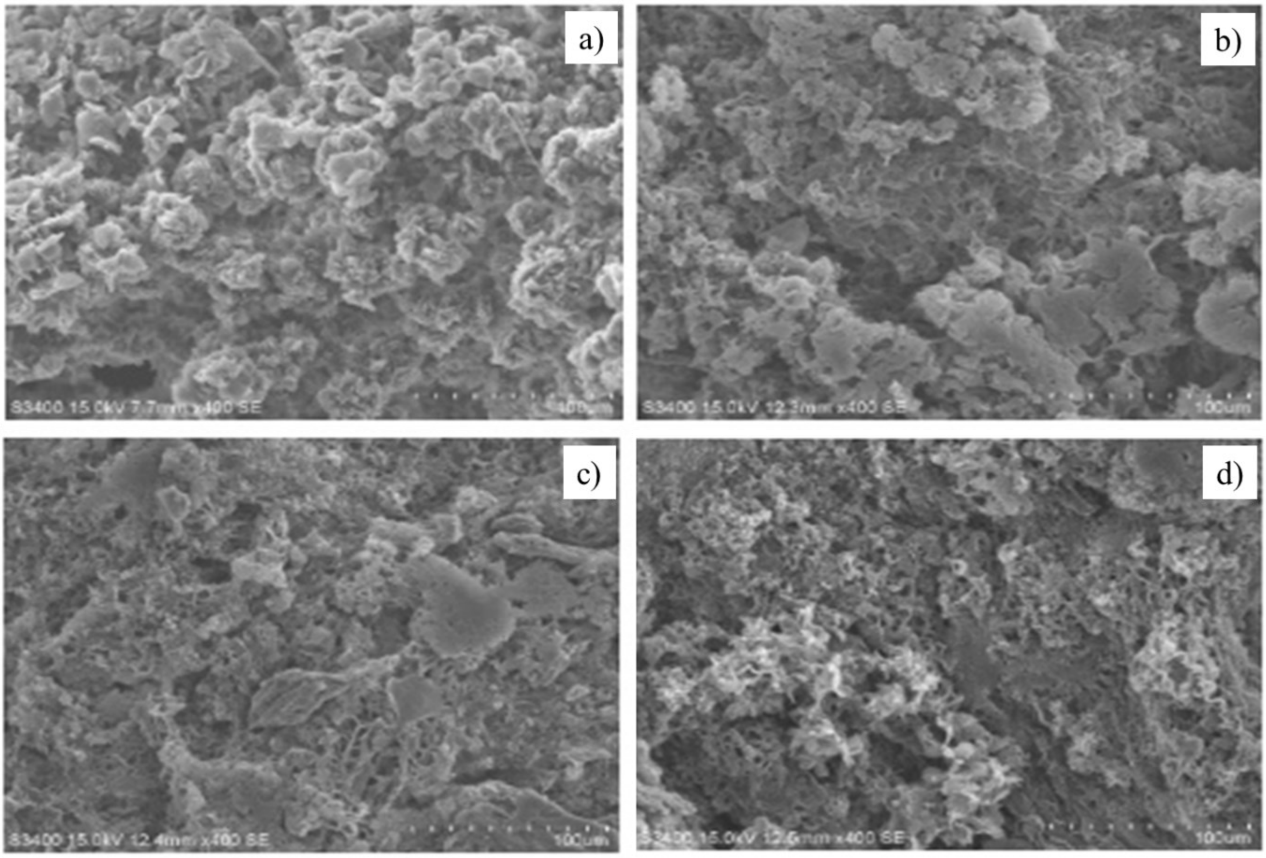

Figure 7. SEM micrographs of polyethylene a) PE, b) PE-Cellulose/Zr, c) PE-Cellulose/MAO and d) PE-Cellulose/(Zr+MMAO).

linity (c_c) of the obtained samples were investigated using a TGA-DSC technique as the result shown in Table 2. It can be seen that the melting temperatures of all samples were nearly the same in the range between 119 and 122 °C. On the contrary, their crystallinity values considerably varied. The PE from the homogeneous system had the far higher crystallinity than all biocomposites from the heterogeneous systems (with the fillers). This suggests that the presence of the cellulose fillers decreases crystallinity of the polymers, probably by inhibiting the crystallization process during polymerization. The opposite was true for our previous work [8], which was found that the cellulose fillers (bacterial cellulose) enhanced crystallinity to the obtained polymer. Thus, the different types of cellulose differently affect crystallinity of the polymers. In addition, it can be seen that the different immobilization methods also differently affected crystallinity of the polymers. Morillo *et al.* [38] have found that directly immobilizing various kinds of metallocene catalysts onto the $MgCl_2/SiCl_{4-n}(n\text{-}C_6H_{13}O)_n$ filler used for ethylene polymerization led to the higher crystallinity of the polymers compared to the polymers obtained from the homogeneous systems for all kinds of metallocene used. For another work, Panupakorn *et al.* [39] immobilized MAO onto the nanoclays to produce polyethylene nanoclay composites, and found that the presence of the high amount of nanoclay (20 wt.%) decreased crystallinity of the obtained composite compared to the pure polyethylene from the homogeneous systems. Hence, from the mentioned works it may be extracted that immobilizing MAO onto the supports or fillers tends to decrease crystallinity of the polymer (polyethylene) than immobilizing the metallocene, which agree with this study. However, the cause of this phenomenon should be further investigated in more detail.

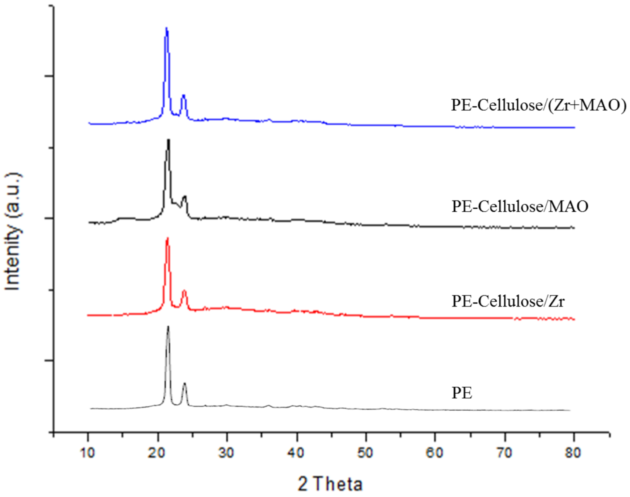

Figure 8. XRD patterns of polyethylene from different methods of immobilization.

4. Conclusion

Three different immobilization methods were used to prepare three different catalytic fillers including Cellulose/Zr, Cellulose/MAO and Cellulose/(Zr+MAO). It was observed that Cellulose/MAO gave the highest catalytic activity among all fillers owing to a crown-alumoxane complex, which caused the heterogeneous system with this filler similar to the homogeneous system. All fillers were well distributed all over the obtained biocomposites as no cellulose characteristic peaks observed in their XRD patterns. Nevertheless, all fillers reduced crystallinity of the obtained biocomposited although they still exhibited the nearly similar melting temperature values, and the main crystal structure indicated to the typical polyethylene was still observed for all obtained biocomposites.

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Table 2. Melting temperature and crystallinity of PE/cellulose biocomposites from various immobilization methods.

Sample	Melting temperature (°C)	Crystallinity[a] (%)
PE	121.8	82.9
PE-Cellulose/Zr	119.8	56.3
PE-Cellulose/MAO	120.1	38.8
PE-Cellulose/(Zr+MAO)	120.0	52.2

[a] Crystallinity was calculated from the equation; %crystallinity = ($\Delta H_{sample}/\Delta H_{100\%}$ crystallinity of polyethylene, 286 J/g)x100

ny (TPE) for providing some chemicals and materials.

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