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Preparation and properties of coral/β-polypropylene biocomposites

Jiaming Xian[1] · Ziqin He[1] · Mingqing Li[1] · Zhidan Lin[1] · Jiaxia Chen[1] · Qigui Yang[1] · Long Xiao[1] · Wei Li[1]

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Abstract In this paper, we present the results of research on the structure and properties of coral/PP biocomposites. Coral powder was chemically treated before use with pimelic acid (PA) through solution method. It was compounded with PP using melt extrusion, and the structures and properties of prepared PP composites were examined. The results show that the coral powder treated with PA performs as an efficient β-nucleating agent, resulting in the maximum K_β value of 0.922 in the composites. It also significantly improved the impact strength by 220.6 % compared with that of the neat PP via improvement in the dispersion and compatibility in PP matrix. The melt crystallization behavior showed that addition of treated coral can promote heterogeneous nucleation.

Keywords Coral powder · Polypropylene · Thermal analysis · Morphology · Mechanical properties · Composites

Introduction

Polypropylene (PP) is a popular commodity thermoplastic polymer with excellent performances, such as good chemical stability, non-toxicity, wear resistance, easy processing, and low cost. It is a crystalline polymer, and there are four common types of PP crystals: α, β, γ, and quasi hexagonal form [1, 2]. The α crystal is the most common and stable one with the best thermal stability, but its impact resistance is not satisfactory. The β crystal is not easy to obtain; it is typically produced via quenching of polymer from the melt [3], inducing shear stress or adding β nucleating agents [4]. The thermal stability of β crystal is good and it offers excellent impact resistance [5, 6], but its rigidity and modulus is smaller than those of α crystal. Due to the increasingly scarce of oil and gas resources, looking for a method to reduce the cost and promote the properties of PP product is very imperative. Addition of inorganic fillers to PP is one of the effective ways to enhance its performance for various applications.

Calcium carbonate [7, 8] is a kind of rigid filler that can induce formation of α crystal in PP [9], while reducing the β crystal content. In order to overcome this problem, researchers found that chemical surface treatment of calcium carbonate particles with pimelic acid (PA) produces pimelic acid calcium that can induce PP to form β crystals [10–13]. This phenomenon will not only enhance the rigidity and impact resistance of the composites but also reduces the production costs.

However, sedimentary fossils, an important source of calcium carbonate, are limited to run out; therefore, we must find other green renewable alternatives. Biomass calcifications [14] are undoubtedly good choices as replacement for the sedimentary fossils that have become a hotspot of study in recent years. Lin have used eggshell [15], shell [16], and monetaria moneta [17] as fillers to prepare β-PP bio-composites, and researches show that all these biomass calcifications can induce PP to form β crystals after heat treatment or surface modification. Coral is one of the representatives of biomass calcifications, which is coral bone debris with short formation period, environmentally friendly, and renewable. Its main component is calcium carbonate, but it includes a small amount of organic matters. Coral is generally used as ornaments, in

✉ Zhidan Lin
linzd@jnu.edu.cn

[1] College of Science and Engineering, Jinan University, Guangzhou 510632, People's Republic of China

which its processing wastes and the rejected products are usually discarded or directly buried, resulting in adverse effects on the environment.

In this research work, we used the abandoned coral as filler, which on the one hand can make coral to reach its maximum utilization and respond to the environmental concerns, and on the other hand can improve the performance of PP and reduce the production costs. Therefore, we designed experiments; coral powder was obtained through crushing abandoned coral and then was treated with PA in a solution method to produce a rigid filler and a β-nucleating agent for PP. To verify the effects of coral chemical treatment on PP, we examined the crystalline form, crystallization melting behavior, non-crystalline dynamics, mechanical properties, and microstructure of prepared PP composites.

Table 1 Composition of coral powder/PP composites in mass/%

Sample	PP	C	CA	CB	CC	CD
PP	100	–	–	–	–	–
PP99C1	99	1	–	–	–	–
PP97C3	97	3	–	–	–	–
PP95C5	95	5	–	–	–	–
PP90C10	90	10	–	–	–	–
PP99CC1	99	–	–	–	1	–
PP97CC3	97	–	–	–	3	–
PP95CC5	95	–	–	–	5	–
PP90CC10	90	–	–	–	10	–
PP95CA5	95	–	5	–	–	–
PP95CB5	95	–	–	–	5	–
PP95CD5	95	–	–	–	–	5

Experimental

Materials

A commercial grade isotactic PP (F401, MFR of 3 g/10 min at 230 °C) was supplied by Sinopec Yangzi Petrochemical Company, China. Coral was obtained from aquatic product market. Chemical grade PA was purchased from Shanghai Hongsheng Industry Company, China. Analytical grade acetone was provided by Guangzhou Chemical Reagent Factory, China.

Preparation of PA-treated coral

The coral was crushed using a high-speed crusher and then was screened with a 200-mesh sieve to obtain coral powder (denoted as C), which size ranged from 1 to 20 μm. Pimelic acid was dissolved in acetone, making a 10 % solution. Coral powder with various amounts of PA (the ratios of coral/PA were 100/1, 100/2, 100/3, and 100/5) was mixed in the acetone solution for 1 h. Subsequently, acetone was vaporized in 12 h inside a vacuum oven at room temperature to obtain various samples of PA-treated coral, denoted as CA, CB, CC, and CD, respectively.

Preparation of PP composites

After adequately drying in a vacuum oven at 80 °C, PP, untreated and PA-treated coral powder were mixed according to the compositions presented in Table 1. Then, the mixtures were homogenized and compounded using a twin-screw extruder to obtain coral/PP composites with various coral contents. The extrusion temperature was set between 180 and 215 °C, and the screw speed was adjusted at 120 rpm.

DSC examinations

The crystallization behavior and melting characteristics of coral/PP composites were carried out with a TA DSCQ10 differential scanning calorimeter (DSC). The temperature and the enthalpy were calibrated with indium at various rates. About 5 mg of the sample was weighed very accurately and heated up to melting temperature of 220 °C and held for 5 min to remove any effects of the thermal and mechanical history. After pre-melting, the samples were cooled to 100 °C at a rate of 10 °C min^{-1} for crystallization behavior observations and then reheated to 220 °C at a rate of 10 °C min^{-1} for melting behavior and polymorphism investigations. All DSC curves in this paper were normalized.

WAXD characterization

The wide-angle X-ray diffraction (WAXD) examinations were performed on the specimens cut from the mechanical testing specimens. The WAXD experiments were conducted with a Rigaku Geigerflex Model D/Max-III A rotating anode X-ray diffractometer. Graphite monochromatic Cu-Kα radiation was used as a radiation source. The scanning range was 5°–40° with the rate of 4° min^{-1} and a step length of 0.02. The β crystal content of PP was determined according to standard procedure described in the literature using Eq. (1) [18]:

$$K_{\beta} = H_{\beta}(300)/\left(H_{\beta}(300) + H_{\alpha}(110) + H_{\alpha}(040) + H_{\alpha}(130)\right) \tag{1}$$

where $H_{\Omega}(h\ k\ l)$ denotes the intensity of respective $(h\ k\ l)$ peak belonging to phase Ω.

Mechanical properties testing

Tensile, flexural, and impact tests were carried out according to ASTM standard methods. For each type of composite, five specimens were tested and the average values were reported. Tensile tests were conducted according to ASTM Standard D 638 using Type V specimen on a universal testing machine (Zwick/RoellZ005, Zwick Roell Testing Machines) at a crosshead speed of 50 mm min^{-1}. Static flexural tests were carried out according to ASTM Standard D 790 using the same testing machine mentioned above at a crosshead speed of 2 mm min^{-1}. Notched Charpy impact strength tests were conducted according to GB/T 1043 Standard method using a universal impact testing machine (ZBC-50, China Shenzhen SANS Testing Machine), and the notches in the specimens were made with a gear cutting machine.

SEM observations

The fracture surfaces of the specimens broken in the impact testing were sputter coated with gold before examinations with scanning electron microscope (SEM). The surface morphologies of the composites were observed on a Philips XL-30 ESE microscope with an acceleration voltage of 15 kV.

Results and discussion

Crystallization and melting behavior results

The thermodynamic parameters presented in Table 2 and Fig. 1 reveal that the crystallization peak temperature increases with increasing the amount of coral, from 117.8 °C for PP to 121.4 °C for the PP composite containing 10 % coral powder. This observation indicates that the coral powder plays a significant role in heterogeneous nucleating of PP and promotes its crystallization process. The melting peak temperature slightly increased with increasing coral content, but the variation was small. The melting peak appears at 163 °C, which is a typical characteristic of α crystallization peak. This result shows that the untreated coral powder does not perform well in the nucleation of β crystal.

Table 2 Thermodynamic parameter of coral powder/PP composite materials

Sample	T_c/°C	ΔH_c/J g^{-1}	T_m/°C	ΔH_m/J g^{-1}
PP	117.8	125.2	162.7	113.4
PP99C1	118.2	111.6	163.2	100.2
PP97C3	118.6	104.3	163.6	104.1
PP95C5	119.7	109.3	163.1	108.5
PP90C10	121.4	104.0	163.6	106.6
PP95CA5	120.2	98.8	151.7, 163.9	58.3, 9.7
PP95CB5	118.4	105.6	154.0, 165.1	59.8, 5.2
PP90CC10	119.2	151.4	153.8, 164.8	104.8, 5.5
PP95CD5	119.7	138.9	151.8, 164.0	92.5, 9.9

The DSC curves of PP composites containing same amounts of coral treated with different amount of PA (Table 2 and Fig. 2) indicate that the crystallization peak temperature reaches to maximum value basically after addition of 5 % coral sample A. The peak temperature changed slightly with increasing PA content afterward, illustrating that the treated coral still plays an important role in the heterogeneous nucleation. But it is obviously different in the fusion curve compared with that presented in Fig. 1. The melting peak of β crystal clearly appears at about 152 °C, whereas the melting peak of α crystal apparently decreased. This observation indicates that the treated coral powder strongly supports the nucleation of β crystal and the ratio of the melting peaks of β crystal and the α crystal gradually increased with increasing the amount of PA. So, coral powder can be an excellent additive promoting the crystal nucleation.

WAXD analysis

In the WAXD spectrograms of coral/PP composites (Fig. 3), neat PP only showed the absorption peaks at 13.9°, 16.7°, and 18.3°, corresponding to the crystal faces of (110), (040), and (130) for α-crystal form of PP. This experimental observation indicates that the used neat PP was only composed of α crystal. But when a certain amount of coral treated with PA was added, the new absorption appeared at 16.2°. This absorption peak corresponds to the β-crystal form (300). Moreover, this absorption peak obviously replaced that of α crystal of neat PP. It illustrates that the addition of treated coral powder let the PP have crystallization behavior of β crystal, making it as the main crystal form in the polymer structure. Figure 4b clearly reveals that with increasing PA content, the peak height of β crystal gradually increases. By contrast, the peak height of α crystal gradually decreases. The specific amounts of β crystal calculated using Eq. (1) are presented in Table 3. It shows that the untreated coral did not influence the nucleation of β crystal, which was verified by the previous melting behavior observations. For the coral powder treated with the same amount of PA, when its content in the composite increased, the β-crystal content gradually increased and reached to the maximum value of 0.922 at the coral content of 10 %. When the coral powder treated with different amounts of PA, by increasing the PA quantity, the content of the β-crystal phase clearly increased. This

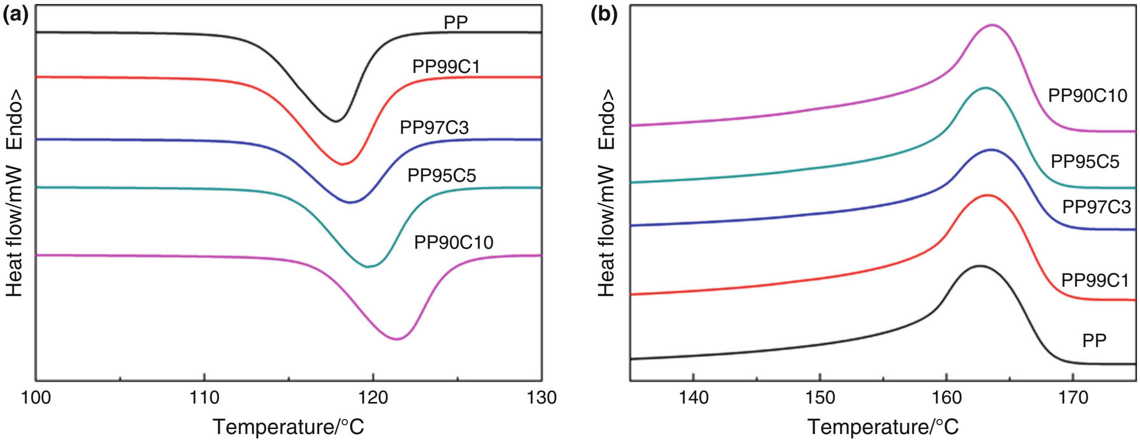

Fig. 1 DSC **a** crystallization and **b** melting curves of the PP composites containing different amounts of untreated coral powder

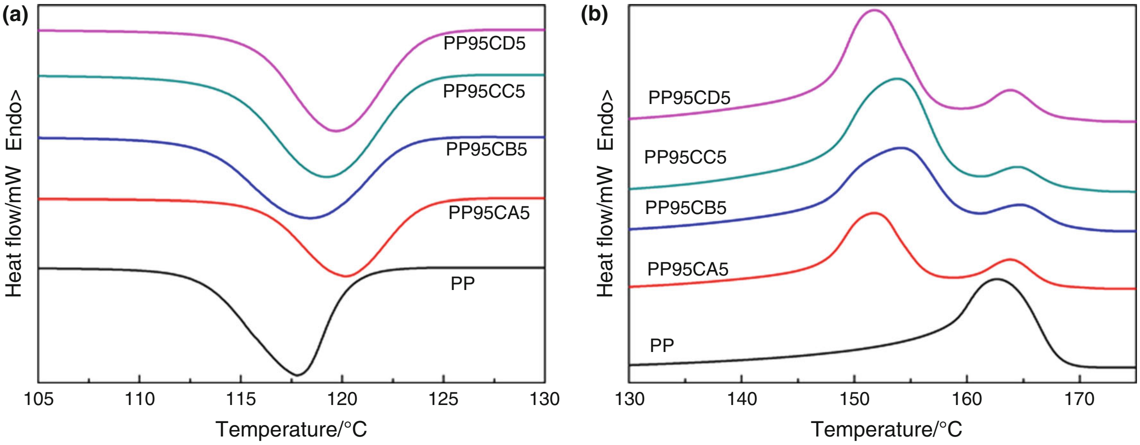

Fig. 2 DSC **a** crystallization and **b** melting curves of the PP composites filled with the same amount of coral powder treated with different amounts of PA

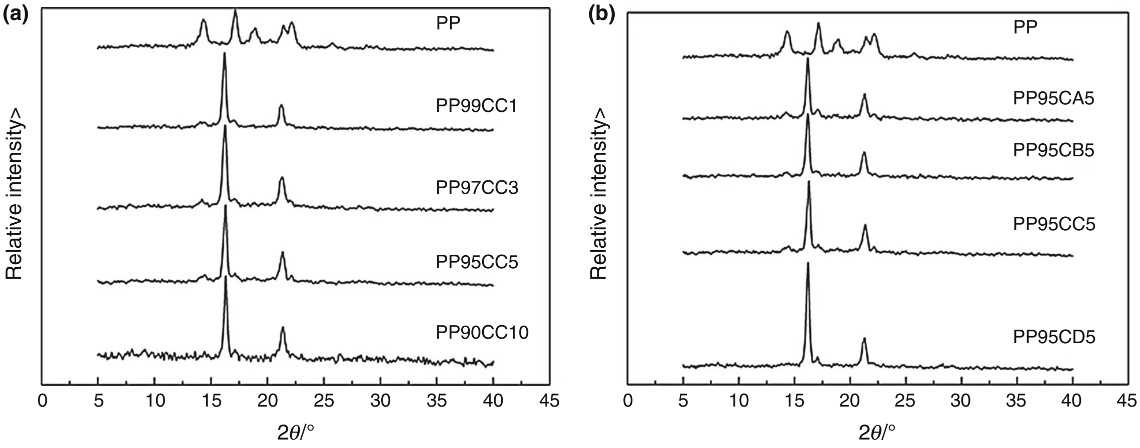

Fig. 3 WAXD spectrograms of **a** the PP composites containing different amounts of coral powder treated with the same amount of PA and **b** the PP composites filled with the same amount of coral powder treated with different amounts of PA

observation is due to the chemical reaction of coral powder with PA and production of pimelic acid calcium on the powder surface, which plays a stronger role in the β nucleation of PP. Presence of more pimelic acid calcium in the composite leads to further β nucleation. In Lin's researches, the maximum K_β value of eggshell/PP, shell/PP,

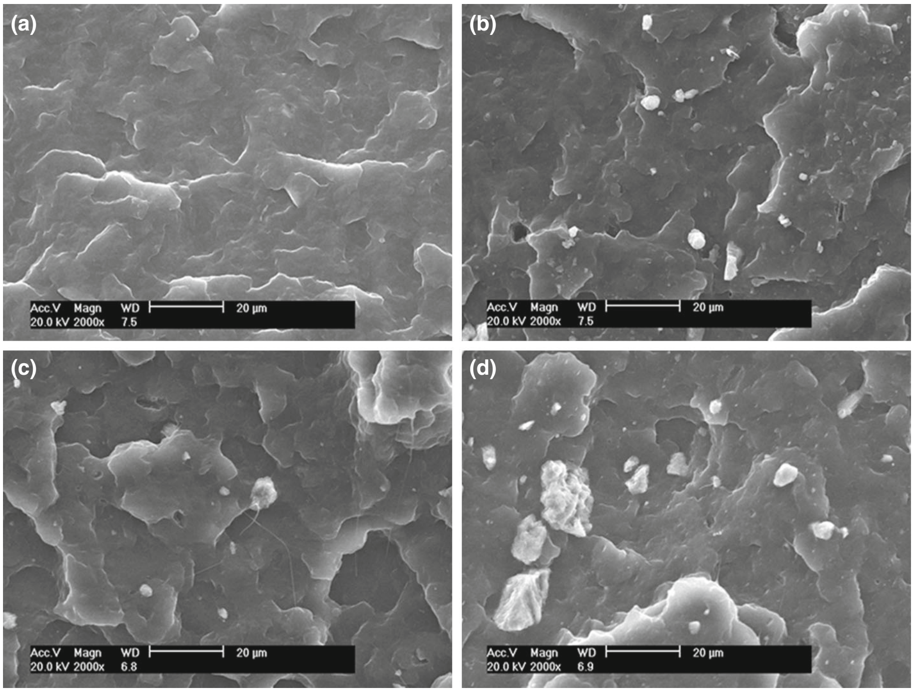

Fig. 4 Micrographs of coral/PP composites: **a** neat PP, **b** PP97C3, **c** PP97CC3, **d** PP90CC10

Table 3 K_β of coral powder/PP composites

Sample	K_β
PP	0.064
PP99C1	0.065
PP97C3	0.071
PP95C5	0.071
PP90C10	0.069
PP99CC1	0.851
PP97CC3	0.820
PP95CC5	0.850
PP90CC10	0.922
PP95CA5	0.803
PP95CB5	0.845
PP95CD5	0.920

and monetaria moneta/PP bio-composites is 0.99, 0.566, and 0.801, respectively. Thus, it can be concluded that the coral powder treated with PA is a fine and effective nucleating agent of β crystal in PP.

Mechanical properties analysis

Many studies have shown that the stiffness of PP can be enhanced with addition of inorganic hard particles. The coral powder, mainly consisting of calcium carbonate, can enhance rigidity of PP. The notched impact strength of neat PP was measured as only 34.4 J m^{-1} (Table 4); however, when PP was filled with untreated coral powder, the impact strength increased along with the increase in the amount of added coral. When the content of coral powder was 10 %, the impact strength reaches 54.0 J m^{-1}, 57 % raise. This observation illustrates that the coral particles enhance the toughness of the neat polymer via preventing the crack propagation under external stress, thus improving the impact properties. The impact strength of the composites was obviously improved through treatment of coral with PA. The maximum value of impact strength was found as 110.3 J m^{-1}, 220.6 % larger than that of neat PP. This improvement is due to the treatment of coral powder that performs as β-crystal nucleating agent, inducing PP to produce more β crystals, and in this way enhancing the impact resistance of the composites. But the impact strength of PP90C10 was found only 82.4 J m^{-1} as its K_β was obtained as 0.922. It is because when there is more coral powder in the composite, the particles easily agglomerate in the PP matrix, producing more defects and decreasing the impact strength. In addition, we observed that the tensile strength as well as the bending strength of the composites can be improved using untreated coral powder, whereas these properties declined after the treatment of coral as the β crystal is weaker than the α crystal. However, the bending modulus increased to a certain degree and reached to 1213.3 MPa. As for the elongation at break, the treated coral/PP composites showed significant increase from 97.2 % for neat PP to a maximum value of 160 %, with a 62.8 % increase. This observation indicates

Table 4 Mechanical properties of coral powder/polypropylene composite material

Sample	Impact strength/ J m^{-1}	Tensile strength/ MPa	Tensile modulus/ MPa	Elongation at break/%	Flexural strength/ MPa	Flexural modulus/ MPa
PP	34.4 ± 1.7	33.0 ± 0.4	446.4 ± 25.6	97.2 ± 7.4	32.9 ± 0.4	1020.0 ± 28.2
PP99C1	38.1 ± 2.1	33.3 ± 0.8	484.7 ± 20.5	78.0 ± 17.9	33.0 ± 0.3	1023.0 ± 38.4
PP97C3	41.8 ± 2.9	33.6 ± 0.6	487.2 ± 7.3	86.4 ± 8.9	33.2 ± 0.4	1005.0 ± 7.0
PP95C5	47.6 ± 1.4	33.1 ± 0.7	458.2 ± 21.3	92.0 ± 21.7	33.1 ± 0.2	1090.0 ± 17.3
PP90C10	54.0 ± 2.3	31.9 ± 0.5	463.0 ± 21.9	91.8 ± 26.6	33.6 ± 0.3	1140.0 ± 43.5
PP99CC1	97.6 ± 7.6	30.2 ± 0.8	425.8 ± 3.9	140 ± 15.8	29.2 ± 0.4	993.0 ± 10.4
PP97CC3	106.2 ± 5.4	30.1 ± 0.3	434.6 ± 15.8	153.3 ± 58.2	30.8 ± 0.7	1010.3 ± 64.0
PP95CC5	101.3 ± 4.8	31.2 ± 0.6	454.5 ± 26.5	160.0 ± 16.7	31.1 ± 0.5	1036.7 ± 32.1
PP90CC10	82.4 ± 6.1	31.3 ± 0.4	490.4 ± 13.5	130.0 ± 18.7	33.9 ± 0.3	1213.3 ± 37.8
PP95CA5	101.6 ± 6.9	29.9 ± 0.2	426.0 ± 9.3	158.0 ± 19.2	30.3 ± 0.1	985.3 ± 21.5
PP95CB5	100.9 ± 5.3	29.9 ± 0.2	444.6 ± 22.9	126.0 ± 25.1	31.2 ± 0.4	1076.6 ± 32.1
PP95CD5	110.3 ± 6.7	29.5 ± 0.6	439.2 ± 17.2	125.0 ± 21.6	31.1 ± 0.1	1015.3 ± 67.1

that β crystal can improve the toughness of composites. In other words, the coral powder treated with PA can greatly improve the mechanical properties of PP (toughness and rigidity), especially the antishock performance when it is blended with PP.

Microstructural observations

Composites can promote their mechanical properties via improvement in particles distribution or improvement in the compatibility between filler particles and matrix [9]. The micrograph in Fig. 4a reveals a flat structure for the section. This morphology is owing to the homogeneous nucleation mechanism in the cooling process of PP, leading to the production of α crystals. In this crystalline microstructure, the apparent crystal boundary extends the shock crack without any obstructions, resulting in a brittle material.

Figure 4b shows the cross-sectional SEM micrograph after addition of 3 % untreated coral powder in which the particle size is smaller and the particles are uniformly distributed in the PP matrix. Despite this beneficial point, the compatibility between coral powder, as an inorganic substance and essential component of the composite, and the PP matrix is not good. Segregation phenomenon occurs, and the particles relatively easily come off the matrix. Some holes on the section of the matrix were also observed.

Figure 4c reveals the microstructure of PP composite containing 3 % treated coral powder in which the flatness of the surface reduced and the compatibility between particles and the matrix greatly improved. There was no shedding phenomenon, but drawing thread phenomenon can be found. The reason behind this microstructure is that the surface of the treated coral powder includes pimelic acid calcium that promotes compatibility of filler particles with PP matrix. Moreover, the pimelic acid calcium demonstrates as an efficient β-crystal nucleating agent. It induces PP to produce a great quantity of β crystals. This kind of crystal has small size and inconspicuous boundary [17]. The cracks are extended with winding paths that make a rough and uneven fracture surface. Therefore, the shock resistance of the composite material improves. The fracture surface micrograph of composite containing 10 % treated coral (Fig. 4d) shows larger particles and less uniform dispersion. Because the original coral powder had small particles and high surface energy, when larger amounts of powder were added, agglomerate phenomena were resulted in the PP matrix. This issue supports the observation that at higher filler contents, the shock resistance deceases.

Conclusions

Coral powder is an excellent rigid inorganic filler that can be added to PP to improve the rigidity and strength. The coral powder treated with PA is tremendous filler that not only enhances the stiffness and toughness of PP but also can act as an efficient β-crystal nucleating agent. It promotes the formation of β crystals well. The amount of produced β-crystal phase in the polymer is codetermined by both coral powder and PA contents. In addition, the surface-treated coral can improve the dispersion of particles in the PP matrix and promote the compatibility between them. With consideration of all conditions, the optimal mass ratio of PP/C/PA was found as 95:5:0.25. At this composition, the content of the β crystal was obtained as 0.92, the impact strength as 110.3 J m^{-1}, an increase of

220.6 % compared with that of neat PP. Therefore, filling PP with the treated coral powder results in a fine composite material in a feasible way that can not only reduce the production cost but also provide a solution for protection of the environment.

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