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## Preparation and characteristics of polyacrylic ester-based water-free powder coatings in supercritical carbon dioxide

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**ABSTRACT**: Powder coating for dry coating technique of paper as the promising method has attracted more and more attentions in recent years due to its advantages in reducing the dosage of water and saving energy compared with conventional coating. This study focused on the *in situ* polymerization of methyl methacrylate (PMMA) under a water-free condition in supercritical carbon dioxide in the presence of inorganic kaolin. The effects of varying the concentrations of the monomer, initiator, and stabilizer on the molecular weight and morphology of the resultant PMMA were investigated and discussed. Then the powder coating was systematically evaluated and characterized by gel permeation chromatography, scanning electron microscopy, Fourier transform infrared spectroscopy, and thermogravimetric analysis. Meanwhile, the feasibility of manufacturing PMMA/kaolin powder coatings was explored, and the mechanism of polymerization and the thermal degradation kinetics of powder coating were studied. The experimental results showed that the properties of PMMA as a film former were suitable with the molecular weight and narrow molecular weight distribution close to that in conventional coating when the concentration of monomer was about 10 wt %, concentration of initiator ~1–1.5 wt % and stabilizer about 10 wt % with respect to monomer. Moreover, the interfacial bonds and dispersion situation of polyacrylic ester-based water-free powder coating particles were fairly well, the powder coating possesses good film-forming property combined with outstanding thermal-stability performance. The combination of these characteristics makes PMMA/kaolin powder coating an excellent candidate for dry coating technique of paper applications. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42439.

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#### INTRODUCTION

The dry coating technique of paper substrate can potentially eliminate the drying process and obtain a desired surface equal to those achieved by conventional coating processes. This method is advantageous in saving energy and formulating an efficient process for the manufacture of coated paper. The hydro-soluble coating suspension (usually with 30-70% solid content) is first transferred on the surface of a base paper by a coater before being evaporated by dryers during the conventional production of coated paper. The drying process increases the operation costs and induces a risk for particle aggregation of the coating suspension. The quality of the paper may deteriorate because of the rewetting-drying process. For instance, the superficial physical properties of the formed coating layer will vary because of the binder migration up to the coating layer surface or down to the base paper. Thus, Maijala et al. proposed a dry surface treatment (DST) technique for paper-based substrates.<sup>1-3</sup> The DST method primarily involves the application of powder coating on the paper surface and fixation of the coating layer in an immediate thermo-mechanical press and smoothening phase. A schematic diagram of the unit is shown in Figure 1.<sup>2</sup> The thermoplastic binders of powder coating should be softened and deformed to bond the pigment particles together and anchor the coating layer to the substrate.<sup>4–6</sup>

Compared with the conventional coating preparation and the drying of the wet-coated paper, the powder-coating process can be achieved without contacting the base paper and can reduce the energy requirement for drying. Without rewetting the paper, the negative effects on the quality of the paper can be reduced or even avoided.<sup>7,8</sup> Additionally, the grades of various pigments are readily available in the dry state, which are either ground or prepared under dry conditions such as GCC, kaolin, talc, etc.<sup>9,10</sup>

Different supercritical fluids as media have been proposed to manufacture the powder coating to reduce cost and improve the quality of the coated paper, avoiding the use of water or

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Figure 1. Schematic diagram of the DST unit with two sides of electrostatic deposition.

organic solvents.<sup>11,12</sup> As an alternative to water, hydrocarbon, or halocarbon solvents, supercritical fluids, especially supercritical carbon dioxide (sc-CO<sub>2</sub>), have obvious advantages as polymerization media and as processing aids to modify products.<sup>13–15</sup> The viscosity and diffusivity of sc-CO<sub>2</sub>, a cheap, nonflammable, and environmentally acceptable solvent, is relatively easy to alter by varying temperature and pressure (the sc-state above 304 K and 7.38 MPa).<sup>16</sup> Given the solubility of monomers and polymers in sc-CO<sub>2</sub>, various polymer synthesis methods in sc-CO<sub>2</sub> are available such as solution, precipitation, dispersion, and emulsion polymerizations.<sup>17,18</sup> In solution polymerization, the stabilizer contributes to the *in situ* stabilization of the polymeric particles formed. The attachment or anchoring of the powder coating is either through chemical grafting or physical adsorption, which implies that different stabilizers are required for different polymers.

Most studies in this field have focused on the free radical polymerization of vinyl monomers, especially the synthesis of polymethylmethacrylate (PMMA) and polystyrene.<sup>19,20</sup> In this study, we



**Figure 2.** Effect of varying initiator AIBN concentration on  $M_w$  and MWD of PMMA.

investigated the polymerization system of MMA with hydroxylterminated polydimethylsiloxane (PDMS) as stabilizer and 2,2azo-bis-isobutyrylnitrile (AIBN) as initiator in the presence of kaolin as pigment in sc-CO<sub>2</sub> to prepare the particles of powder coatings for the DST of paper. The resultant powder hybrid particles were investigated for the structure, the distribution of the components as well as the performance of thermal stability.

#### EXPERIMENTAL

#### Materials

The materials used in the study are listed in Table I. MMA was purified by vacuum distillation, and AIBN was prepared through recrystallization with ethanol, Kaolin, CO<sub>2</sub>, AIBN, and hydroxyl-terminated PDMS were directly used as received.

#### Preparation of Powder Coatings Using Supercritical Fluids-Based Techniques

Supercritical carbon dioxide (sc-CO<sub>2</sub>) has attracted more attentions not only as polymerization media but also as processing aids. The advantage of working in the sc-state of the medium or the solvent is the ability to tune the viscosity and diffusivity of the fluid by varying the temperature and pressure. With CO<sub>2</sub> the sc-state is relatively conveniently achieved and allows treatment of thermally sensitive materials.<sup>21–23</sup> Generally, CO<sub>2</sub> is a good solvent for small nonpolar and weakly polar molecules.<sup>24</sup>

Table	I.	Materials	Used	in	This	Experiment
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Materials	Note	M <sub>w</sub> (g/mol)	Size (µm)
MMA > 99%, Gangzhou, China	Monomer	100	-
CO <sub>2</sub> 99.99%,Gangzhou, China	Medium	44	-
AIBN, Gangzhou, China	Initiator	164	-
Hydroxyl-terminated PDMS, Alfa Company	Stabilizer	4000	-
Kaolin, Gangzhou, China	Pigment	-	0.2

Note: M<sub>w</sub>: molecular weight.

The reaction was performed using a 15 mL pressure vessel equipped with a magnetic stirrer and facilities for monitoring temperature and pressure. The reactor was first charged with the monomer, kaolin, stabilizer, and initiator according to a preset ratio before being stirred and sealed.  $CO_2$  was added at room temperature to a preset monomer/ $CO_2$  ratio. The pressure in the vessel was initially between 8 and 10 MPa. After the pressure was stabilized, the vessel was heated in an oil bath. When the reaction was close to completion, the reactor was cooled in a water bath. The pressure was subsequently reduced to the initial level, and  $CO_2$  was vented. The resultant products were collected and weighed to determine the gravimetric yield.

#### **Examination of Powder Coatings**

Prior to all examinations, the powder coatings containing aggregates were dispersed to suitable sizes by grinding at room temperature. The bonding of powder coatings was studied by Fourier-transform infrared spectroscopy (FTIR). The morphology of those powder coatings was characterized by SEM. The molecular weight  $(M_w)$  of PMMA was determined by GPC and the thermal properties were investigated by thermogravimetric analysis (TGA).

#### Calculation of the MMA Monomer Conversion Ratio

MMA monomer conversion ratio C refers to the ratio of the quality of monomer participate in reaction and the monomer total quality  $W_0$  before reaction, it was obtained by weighing method.

$$C = (W - W_1 - W_2) / W_0$$

where *W* is the total quality including vessel reactor and reactive material,  $W_1$  is the total quality of the rest of the material except monomer MMA before reaction, and  $W_2$  is the quality of the vessel reactor.

### The Measurements of PMMA Relative Molecular Weight and Its Distribution

The relative molecular weight and distribution of the polymerization products of PMMA was measured by Gel Permeation Chromatography, the GPC measurements were performed on a Agilent series 1100 HPLC equipped with a PL gel 104 Å mixed C column with THF as eluent. An UV detector set at 254 nm was used. The solution injected had a concentration of 0.3 wt %.The flow rate of mobile phase THF is 1 mL/min, the injection amount is 30  $\mu$ L, and the column temperature is 30°C. The molecular weights were determined using a calibration curve obtained from polystyrene standards.

#### Scanning Electron Microscopy (SEM) Analysis

A SEM was used to examine the surface image of the resultant powder coating. The samples were fixed to a metal-base specimen holder using double-sided, sticky tape. The fixed samples were coated with  $\sim$ 30 Å of Au/Pd, and were then observed using a S-3700 SEM.

#### FT-IR Analysis

The chemical structures of products were performed on a VEC-TOR33 FTIR spectrophotometer using a standard KBr pellet technique. Each spectrum was recorded with 25 scans in the frequency range  $4000-400 \text{ cm}^{-1}$  with a resolution of 4 cm<sup>-1</sup>.

**Table II.** Effect of Varying Monomer AIBN Concentration on the  $M_w$  and Molecular Weight Distribution (MDW) of PMMA

Entry	MMA (mass/g)	Yield (%)	M <sub>n</sub> of PMMA	M <sub>w</sub> of PMMA	MWD
1	0.70	63.96	39,600	50,400	1.27
2	1.00	82.08	49,200	56,600	1.15
3	1.25	87.06	55,100	61,000	1.11
4	1.50	87.92	63,900	67,600	1.06
5	1.75	93.35	42,900	50,900	1.19

#### **TG** Analysis

TGA was carried out for studying the thermal stability of the PMMA/kaolin powder coatings. A TGA Q500 instrument was used to record weight loss within the range of room temperature to 800°C, with a heating rate of 10°C/min. The flow rate of nitrogen is 40 mL/min.

#### **RESULTS AND DISCUSSION**

#### Effect of Monomer Concentration on Polymerization

Choosing MMA as the monomer to synthesize acrylic resin for powder coatings, because MMA could improve hardness and tensile strength of the coating film, and endow the coating film with excellent heat resistance. The monomer concentration of MMA was varied from 3.3 to 11.7 wt % with respect to  $CO_2$ (0.7–1.75 g in a 15 mL vessel) to investigate its effect on PMMA. Experiments were conducted at 65°C and more than 12 MPa, kaolin as the pigment with the same weight of MMA, AIBN as the initiator (1 wt % with respect to MMA), hydroxyl-terminated PDMS as stabilizer (10 wt % with respect to MMA), and 10 h reaction time. The results are listed in Table II.

Table II shows that the yield of PMMA increased from 63.96 to 93.35% when the monomer concentration changed from 0.7 to 1.75 g. Additionally, the yields at lower monomer concentrations should be slightly lower, because the small-scale experiment tends to exaggerate the effects of the loss of the PMMA (Entries 1 and 2) from the pressure vessel. With an increase in monomer concentration, the yield of PMMA distinctly increased to the desired value of 93.35% with 11.7 wt % concentration of MMA. This phenomenon is caused by the increased solvency of the medium for the resultant polymer and the stabilizer after additional monomers were added to the reaction system, more free radical active centers were received, the more monomers involved in free radical polymerization, as a result, the risk of collisions between MMA monomer molecules and the free radical activity center was increased, which in turn allowed the formation of larger molecules. The  $M_w$  slightly changed with an increase in monomer concentration, and its distribution varied similarly with narrow values, when the concentration of MMA was 10%,  $M_w$  to achieve the maximum of 67600, as well as the MWD of 1.06. After repetitions of experiments, the resulting data are basically identical. The properties of PMMA as a binder were close to those of the other binders that were used in conventional paper coating.<sup>25</sup>



#### Effect of Initiator Concentration on Polymerization

Concentrations of the initiator ranging from 0.5 to 2.5 wt % with respect to monomer MMA were investigated at constant monomer (1.5 g) and stabilizer (0.1 g) concentrations with more than 12 MPa systemic pressure,  $65^{\circ}$ C systemic temperature, and 10 h reaction time. The results are summarized in Figure 2.

Figure 2 shows that as the initiator AIBN concentration increases, the  $M_w$  significantly decreases. The  $M_w$  decreased from ~50,000 to 25,000 when the initiator AIBN concentration changed from 0.5 to 2.5wt %. This phenomenon is due to the increased number of radicals in the reaction medium with an increase in the initiator concentration, which resulted in the formation of more nucleation sites and a decrease in the  $M_w$  of PMMA. Moreover, a decrease in the particle size was generally observed because of the additional nucleation of reactions, which was in accordance with the findings of Liao *et al.*<sup>11</sup>

The MWD of PMMA was affected slightly and increased gradually with an increase in the initiator AIBN concentration, while the initiator AIBN concentration ranged from 1.0 to 1.5 wt %, the MWD of PMMA decreased, and reached the lowest when the initiator AIBN concentration was 1.5 wt %. The phenomenon is because when the initiator AIBN concentration is relatively low, little reaction activity center was got from the thermal decomposition of AIBN, the probability of more MMA monomer participated in the same chain growth is bigger; When the initiator AIBN concentration continued to increase, the corresponding reaction activity center became more, the probability of different monomer participated in the same chain growth deduced, at the same time, the probability of monomer participated in different chain growth increased. With repeated experiments, the result of data highly unified.

The effect of initiator concentration on the  $M_w$  for dispersion polymerization in conventional solvents could be described by the Mayo-Walling equation,<sup>27</sup> where the  $M_w$  was proportional to the inverse of the initiator concentration. The results obtained from the sc-CO<sub>2</sub> medium should be relatively anastomotic with the Mayo-Walling equation.

#### Effect of Stabilizer Concentration on Polymerization

To investigate the effect of PDMS concentration on polymerization, a series of polymerizations were performed over a wide range from 0 to 20 wt % with respect to monomer MMA at constant monomer and initiator concentration with more than 12 MPa, 65°C systemic temperature, and 10 h reaction time. The results are demonstrated in Figure 3.

Figure 3 shows that PMMA was synthesized with a low  $M_w$  in the absence of a stabilizer. A distinct increase in  $M_w$  occurred with an increase in the stabilizer concentration. The MDW first decreased and then increased within a relatively narrow scale when the stabilizer concentration was increased. The phenomenon is due to the solubility of prepolymer in the initial stage of reaction in the supercritical carbon dioxide fluid increasing, which was attributed to the increase of the stabilizer concentration. As a result, the polymer molecular chain growing continually, the MWD decreased; However, when a glut of stabilizer, it



**Figure 3.** Effect of varying stabilizer PDMS concentrations on the  $M_w$  and MWD of PMMA.

would intensify the macromolecular chain of PMMA to intertwine as a result of agglomeration, at last, the MWD decreased. Similar to conventional dispersion polymerization, the radical polymerization started as a one-phase, homogeneous system so that the monomer, stabilizer, and initiator were soluble in the sc-CO<sub>2</sub> medium. However, the resultant polymer is insoluble. Thus, no amphipathic molecule as a stabilizer was adsorbed onto the surface of the dispersed phase, and the resultant polymer readily flocculated and aggregated. With an increasing in the stabilizer PDMS concentration from 0 to 20 wt %, there was a distinct increase in the  $M_w$  of PMMA, because stabilizer serve as a carrier for the polymerization, which indicated an interaction that promoted polymerization. The 10% concentration of stabilizer PDMS was relatively appreciable for the radical polymerization of MMA in the sc-CO<sub>2</sub> medium because of the smallest MDW value of 1.15. Through repeated the experiment many times, the result error is very small, can be thought of as basic consistent.

SEM can provide a more visualized image to understand the change in microstructure. SEM micrographs (Figure 4) also revealed that the particle size of the powder coating could be controlled by stabilizer concentration, and a decrease in diameter was observed [Figure 4(a–c)] with an increase in the stabilizer concentration. These results agreed with those observed for dispersion polymerizations in conventional solvents or for the other stabilizer systems in sc-CO<sub>2</sub>.<sup>23</sup> The optimal diameter of hybrid coating particles observed in [Figure 4(b)] can reach to 1  $\mu$ m when the stabilizer PDMS concentration was 10wt %, the phenomenon can also be seen in Figure 4(d), at this time, the powder particle had an even distribution in size. The result also revealed 10% concentration of PDMS was the optimal, which was consistent with the previous result. It was found that the kaolin granules were able to evenly disperse and embedded in PMMA matrix and did not show conglomeration.

#### Effect of Kaolin on Polymerization to the Powder Coatings

Figure 5 is the scanning electron microscope of PMMA/kaolin and PMMA polymer powder coatings, which were both prepared in medium of supercritical system. Which Figure 5(a,c) for powder coatings added kaolin, while Figure 5(b,d) for



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Figure 4. SEM images of the powder-coating particles prepared using 1% AIBN and (a) 0% PDMS (20 K), (b) 10 wt % PDMS (20 K), (c) 20 wt % PDMS (20 K), and (d) 10 wt % PDMS (7 K). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

powder coatings did not add kaolin. Compared two groups of images, it can be seen that the average particle size of powder coatings [Figure 5(b,d)] did not add kaolin was about 1 microns, and the distribution of particle size was relatively wide, it was the local particle conglomerate problems of powder coating, which made the powder coating particles become larger; While in Figure 5(c), the size distribution of powder coating added kaolin was uniform, the particle conglomerate phenomenon was less serious than Figure 5(d). It suggested that, the presence of kaolin was beneficial to uniform distribution of the PMMA resin particles synthesized in supercritical system.

#### **FTIR Analysis**

FTIR spectroscopic analysis is performed to determine chemical structuresl in various powder coatings. The FTIR spectra of the pure PMMA, kaolin, and PMMA/kaolin powder coatings are illustrated in Figure 6. A sharp peak is found at 1734 cm<sup>-1</sup> in the PMMA spectrum (a) that could be attributed to the presence of the C-O stretching vibration. The peaks ranging from 1260 to 1050  $\text{cm}^{-1}$ , 900 to 650  $\text{cm}^{-1}$ , and 3000 to 2900  $\text{cm}^{-1}$ were due to the C-O (ester bond) stretching vibrations, C-H bending vibration, and the C-H of methyl stretching vibrations, respectively. A broad peak was observed at 3445 cm<sup>-1</sup>, which was due to the O-H stretching vibration because PMMA was prepared in the presence of hydroxyl-terminated PDMS in the sc-CO<sub>2</sub>. Compared with spectrum (a), the PMMA/kaolin spectrum (c) also showed a peak at 3441 cm<sup>-1</sup>, but not as intense as spectrum (a). PMMA was inferred to have interacted with kaolin by hydrogen bonding and resulted in the weakening of the O—H absorption peak from PDMS. Similar absorption peaks of the hydroxide radical were also observed in previous literatures.<sup>28,29</sup>

The characteristic absorption peaks from spectra (a) and (b) could also be seen in spectrum (c), and some of the peaks were slightly shifted. For example, the characteristic peak of kaolin moved from 1433 cm<sup>-1</sup> to a high wave-number at 1447 cm<sup>-1</sup>, and the peak from the methyl of PMMA moved from 2954 cm<sup>-1</sup> to a high wave-number at 2962 cm<sup>-1</sup>, which indicated that polymer PMMA and inorganic kaolin were not physically mixed, but bonding interactions existed between them. The specialty was benefit to adjust the binder properties and improve the structure of the coating layer.

#### Thermogravimetric Analysis

The thermogravimetric trace of PMMA/kaolin powder coatings were demonstrated in Figure 7. The DTG curve indicates that the sample weight loss during thermal degradation occurred in four distinct steps. The first degradation step of weight loss could be attributed to the unzipping of PMMA by the initial cleavage of head-to-head linkages with a maximum weight loss of ~7.39% at 157°C. The second degradation step was attributed to the initial  $\beta$ -scission at the vinylidene chain ends followed by unzipping with a weight loss of ~11.5% at 290°C for the composite. The third degradation step was due to the unzipping after random chain cleavage, reaching a maximum weight loss of ~31.94% at 395°C, resulting in the decomposition of the remaining PMMA. The maximum weight loss



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Figure 5. SEM images of powder coatings: (a and c) for PMMA/kaolin; (b and d) for PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

during the final step reached  ${\sim}21.26\%$  at 755°C, which was mainly caused by the degradation and deprivation of inorganic kaolin.

According to the literature,<sup>8,30</sup> the processing temperature of powder coating was about 120°C and the curing temperature was about 200°C, while the maximum weight loss rate temperature of the powder coating was higher than 290°C, and the heat-resisting performance can meet the processing and curing



Figure 6. FTIR analysis of PMMA/kaolin powder coatings.

temperature of the powder coating. Therefore, the thermal stability performance of PMMA/kaolin powder coatings has the ability to satisfy the requirements of paper for dry coating.

## Research on the Thermal Degradation Kinetics of Powder Coating

Studying on the pyrolysis kinetics of the synthesis of resin can be benefit to deeply understand its thermal stability, and it



Figure 7. TGA of PMMA/kaolin powder coatings.



Figure 8. Fitted curves of powder coating during whole temperature range. [Color figure can be viewed in the online issue, which is available at wileyon-linelibrary.com.]

would provide a theoretical basis for the application of synthetic resin. Pyrolysis model through theoretical calculation to simulate the reaction activation energy E, pyrolysis rate, and related kinetic parameters. Pyrolysis model is a good method to explore the pyrolysis kinetics of PMMA synthetic resin. In general, the pyrolysis reaction of synthetic resin is more complex, needs to simplify the processing.

The pyrolysis area of PMMA/kaolin powder coating mainly occurred between 300 and 380°C, therefore, in this period of temperature, according to the Coats-Redfern<sup>31,32</sup> model to study the thermal decomposition kinetics of polymer, and according to the analysis method in related literatures,<sup>33,34</sup> the curve needed to be fitted step by step. The temperature curves between 300 to 340°C and 340 to 380°C were made respectively, and carried on the linear fitting respectively, then the reaction activation energy E of different temperature segment were caculated.

Figure 8 shows the thermal degradation of linear fitting of powder coating between the temperature of 300 to  $340^{\circ}$ C and 340

to 380°C. It can be seen from the Figure, the linear correlation coefficient R received by the curve fitting step by step is very high, especially in the high temperature period, reached to 0.99 or more (Table III). Within the two temperature periods, the reaction activation energy E of PMMA/kaolin powder coating was higher than that of PMMA synthetic resin. The greater of the thermal degradation reaction activation energy of the powder coating, the better of the thermal stability.<sup>35</sup> The adding of kaolin in the reaction system, which improved the thermal degradation reaction energy of PMMA synthetic resin, thus, the thermal stability of the powder coating had been effectively enhanced.

## Study on the Mechanism of Polymerization to Form Products of PMMA/Kaolin Powder Coating Particles

The process of polymerization could be divided into two parts: the first stage is free radical polymerization of MMA, the second stage is the combination of PMMA and Kaolin particles. Figure 9 is the mechanism analysis diagram of the preparation of

Table III. Kinetics Parameters of Powder Coating Within Different Scale of Temperature

Temperature range (°C)	Powder coating	Linear correlation coefficient (R)	Fitting line slope (K)	Activation energy [E (kJ mol <sup>-1</sup> )]
300-340	PMMA	0.9464	-4477.96	-37.2
	PMMA/kaolin	0.9766	-5794.32	-48.1
340-380	PMMA	0.9978	-10596.76	-88.1
	PMMA/kaolin	0.9951	-29578.80	-245.9



Figure 9. Mechanism analysis of polymerization to form PMMA/kaolin powder coating particles.

polyacrylic ester-based water-free powder coatings. AIBN was used as the initiator to trigger the polymerization of MMA under 65°C, less amount of monomer free radicals was generated caused by initiator at initial stage of reaction, which resulted in small probability of termination of polymer chain growth. The chain growth of free radicals and the surface of kaolin had big risk of collision, which was attributed to small size and larger specific surface area of kaolin particle in the reaction system.<sup>36–39</sup> Then the polymer chain growth of free radical grafted on the surface of kaolin, And as the reaction progressing, a good cladding layer on the surface of kaolin was formed by the generated PMMA, the resultant powder hybrid particles were obtained through this process.

#### CONCLUSION

With sc-CO<sub>2</sub> as the medium, an effective and feasible way to prepare powder coatings was achieved. The  $M_w$  and MWD of the PMMA produced depend considerably on the concentration of the reactants, stabilizer, and initiator. The preferable concentration of monomer MMA was 10% in the sc-CO<sub>2</sub> medium system, whereas the preferred concentrations for the initiator AIBN and stabilizer PDMS relative to the monomer were 1% to 1.5 wt % and 10 wt %, respectively. SEM micrographs revealed that the particle size may be controlled by very high stabilizer concentrations, resulting in a decrease in diameter. The FTIR result showed that polymer PMMA and inorganic kaolin were not physically mixed, but bonding interaction existed between these compounds. It was found that PMMA/kaolin powder coating with good thermal properties and appropriate molecular weight and its distribution, it can meet the basic requirements of the dry coating properties. Supercritical carbon dioxide, which is environmental friendly, has aroused much interest in the polymerization of resin as a potential solvent for polymerization reactions, which offers a new way to the preparation of the powder coating for dry coating technology.

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#### REFERENCES

- 1. Juha, M.; Kaisa, P.; Johan, G. Proceedings of the TAPPI 2002 Coating Conference. TAPPI Press: Atlanta, GA, **2002**; p 501.
- Kaisa, P.; Juha, M.; Johan, G.; Mikael, R. Proceedings of the 21st PTS Coating Symposium. PTS: Munich, 2003; p 29b-1.
- 3. Nicholas, Y. H.; Jesse, Z.; Hui, Z.; Hiran, P. Surf. Coat. Tech. 2014, 251, 177.

- 4. Kaisa, P.; Juha, M.; Johan, G.; Mikael, R. Proceedings of the TAPPI 2003 Advanced Coating Fundamentals Symposium, Session 1:2. TAPPI Press: Atlanta, GA, **2003**.
- 5. Dorothea, S.; Matteo, C.; James, D.; James, M. Int. J. Pharm. 2013, 457, 488.
- Mohammadreza, K.; Shahin, A.; Ali, N.; Saeedeh, M.; Mehrzad, M.; Mehdi, A.; Dariush, M.; Ahmad, A.; Hamidreza, A. D.; Ali, A.; Donya, P. G. *Prog. Org. Coat.* 2011, *71*, 173.
- 7. Yang, F.; Shen, J. BioRes. 2013, 8, 3177.
- Barletta, M.; Gisario, A.; Trovalusci, F.; Vesco, S. Prog. Org. Coat. 2013, 76, 244.
- 9. Matjaz, K.; Marta, K.; Gundea; Miran, M.; Anton, H. Dyes Pigments 2003, 57, 235.
- 10. Konraad, D.; Paul, S.; Jurjen, B. Prog. Org. Coat. 2011, 70, 205.
- 11. Liao, X. S.; Yang, R. D.; Qi, Z. R. Acta Polym. Sin. 2010, 9, 1088.
- 12. Cédric, B.; Christine, J.; Antoine, D. Eur. Polym. J. 2014, 61, 45.
- 13. Sameer, P. N.; Francesco, P.; Janssen, L. P. B. M. Prog. Polym. Sci. 2006, 31, 19.
- 14. Clark, M. R.; Kendall, J. L.; DeSimone, J. M. *Macromolecules* **1997**, *30*, 6011.
- Cao, L. Q.; Ma, C.; Wang, J. D.; Chen, P. J. Supercrit. Fluids 2013, 75, 152.
- Libin, D.; Jennifer, Y. K.; George, W. R.; Joseph, M. D. J. Supercrit. Fluids 2009, 47, 447.
- 17. Li, G.; Yates, M. Z.; Johnston, K. P.; Howdle, S. M. *Macro-molecules* **2000**, *33*, 4008.
- 18. Christian, P.; Howdle, S. M.; Irvine, D. J. *Macromolecules* **2000**, *33*, 237.
- 19. Zhao, Q.; Edward, T. Samulski. Polymer 2006, 47, 663.
- Haldorai, Y.; Ha, S. H.; Won, S. K.; Hyun, G. K.; Euh, D. J.; Kwon, T. L. *Eur. Polym. J.* 2008, 44, 2253.
- 21. Ernesto, R.; Giovanna, D. P. Pure Appl. Chem. 2001, 73, 1293.
- 22. Okubo, M.; Fujii, S.; Maenaka, H.; Minami, H. Colloid Polym. Sci. 2002, 280, 183.
- 23. Andrew, I. C. J. Mater. Chem. 2000, 10, 207.
- 24. Kaisa, P.; Juha, M.; Johan, G.; Mikael, R. Prog. Org. Coat. 2004, 51, 257.
- 25. Houssni, E. S.; Altaf, H. Basta. Polymer 1995, 36, 4261.
- Christian, P.; Giles, M. R.; Griffiths, R. M. T.; Irvine, D. J.; Major, R. C.; Howdle, S. M. *Macromolecules* 2000, 33, 9222.
- Barrett, K. E. J. Dispersion Polymerisation in Organic Media; Wiley: New York, 1975.
- 28. Maha, M. I.; Waleed, K. E.; Galal, A. M. N. *Carbohydr. Polym.* **2012**, *88*, 1009.
- 29. Hsih, Y. T.; Weng, K. L.; Nam-Trung, N. Sens. Actuators B. 2010, 151, 133.
- 30. Jing, F.; Hui, Z.; Jesse, Z. Adv. Powder Technol. 2013, 1, 1.
- 31. Yuan, Y.; Pan, M. W.; Yuan, J. W.; Yang, S.; Zhang, L. C. Polym. Mater. Sci. Eng. 2009, 25, 15.

- 32. Peng, Y. X. Chemistry 1996, 7, 55.
- 33. Coats, A. W.; Redfern, J. P. Polym. Lett. 1965, 3, 917.
- 34. Sun, Q. L.; L, W.; Chen, H. K. L, B. Q.; L, X. G. J. Chem. Ind. Eng. 2003, 11, 1598.
- 35. Ricardo, C.; Salvador, N.; Ramón, A.; Ana, G.; Angel, V. *Polym. Degrad. Stab.* **2004**, *85*, 667.
- Long, G. B.; Md, R. I.; Jong, T. K.; Sung, Y. S.; Kwon, T. L. Appl. Surf. Sci. 2012, 258, 2959.
- 37. Park, J. Y.; Shim, J. J. J. Supercrit. Fluids 2003, 27, 297.
- 38. Romack, T. J.; Maury, E. E.; DeSimone, J. M. Polym. Prepr. 1994, 35, 741.
- 39. Fatema, B.; Sindee, L. S. Polymer 2011, 52, 1539.

