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N₂ plasma treatment of pigments with minute particle sizes to improve their dispersion properties in deionized water

Jingjing Zhang[a], Yeong Min Park[a], Xing Yan Tan[a], Mun Ki Bae[a], Dong Jun Kim[a], Tae Hwan Jang[a], Min Su Kim[a], Seung Whan Lee[b] and Tae Gyu Kim[c],*

[a]*Department of Nano Fusion Technology, Pusan National University, Busan, Korea*
[b]*Plasma Technology Research Center, National Fusion Research Institute, 37 Dongjangsan-ro, Gunsan-si, Jeollabuk-do, 54004, Korea*
[c]*Department of Nanomechatronics Engineering, Pusan National University, Busan, Korea*

Pigments with minute particle sizes, such as carbon black (CB) and pigment red 48:2 (P.R.48:2), are the most important types of pigment and have been widely used in many industrial applications. However, minute particles have large surface areas, high oil absorption and low surface energy. They therefore tend to be repellent to the vehicle and lose stability, resulting in significant increases in viscosity or reaggregation in the vehicle. Therefore, finding the best way to improve the dispersion properties of minute particle size pigments presents a major technical challenge. In this study, minute particle types of CB and P.R.48:2 were treated with nitrogen gas plasma generated via radio frequency-plasma enhanced chemical vapor deposition (RF-PECVD) to increase the dispersion properties of minute particles in deionized (DI) water. The morphologies and particle sizes of untreated and plasma treated particles were evaluated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The average distributions of particle size were measured using a laser particle sizer. Fourier transform infrared spectroscopy was carried out on the samples to identify changes in molecular interactions during plasma processing. The results of our analysis indicate that N₂ plasma treatment is an effective method for improving the dispersibility of minute particles of pigment in DI water.

Key words: N₂ Plasma, Plasma treatment, Dispersion, Aggregation, RF-CVD.

Introduction

Minute particles of pigment, including carbon black (CB) and some organic pigments like pigment red 48:2 (P.R.48:2), which can have primary particle sizes as small as a nanometer, have been widely used in coatings, paintings, packing, printing inks, cosmetics, and other applications due to their numerous advantages in terms of light sensitivity, color strength, transparency, lightfastness, brilliance, inherent stability, migration resistance, and so on [1-5]. Furthermore, as these minute pigments possess outstanding properties in terms of heat resistance, oil resistance, acid or alkali fastness, weather fastness, and friction resistance, they can also be widely used in tires and plastics, and as fillers in rubber products [6, 7].

However, interaction forces between the particles (especially the van der Waals forces) in relation to gravitational forces, as well as the collision probabilities of the particles, will increase as particle size decreases and the specific surface area increases [8]. Therefore,

minute particles can easily be aggregated and agglomerated when added to a polymer matrix or a variety of media, due to the van der Waals forces, electrostatic, magnetic forces, sintering bonds and complex configuration [9-11]. The pigment aggregates and agglomerates, with sizes that can reach up to several hundred nanometers, or even a dozen or dozens of micrometers in diameter. This will impact the performance of such materials, including their mechanical properties, surface properties, weather fastness, storage stability, color, and so on [11, 12]. Hence, it is very important to break down the aggregates or agglomerates of minute scale pigments in media during the material fabrication process; that is to say, we need to improve the dispersibility of minute particle size pigments in media during the manufacturing process.

To increase the dispersion of minute particle size pigments, numerous surface treatment methods, mainly physical and chemical methods, have been studied by many researchers. Physical dispersion methods usually consist of ultrasonic treatment, stirring, ball-milling etc. [13, 14], while chemical dispersion methods mainly consist of surfactant surface adsorption [15], surface chemical grafting [16], surface oxidation [17], etc. Physical dispersion methods, which usually adopt mechanical methods to disperse the aggregates or

*Corresponding author:
 Tel : +82-55-350-5648
 Fax: +82-55-350-6547
 E-mail: tgkim@pusan.ac.kr

agglomerates, are of low cost and thus are suitable for large-scale production. However, the dispersion rate tends to be low and secondary agglomeration occurs easily [18]. Therefore, physical methods are usually used in support of other methods [19]. Chemical dispersion methods are stable, but cause damage to particle structures and thus environmental pollution [20]. Therefore, preparing stable dispersions of minute particles in aqueous medium using low-cost, technically straightforward and environmentally friendly methods is of great importance and urgently required.

Plasma surface treatment has developed quickly over recent years due to the rapid reaction time, low cost, absence of organic residue, environmental friendliness, and ease of functionalizing various functional groups [21]. Furthermore, many scholars have made progress in the study of the influence of oxygen plasma surface treatment on the dispersibility of minute particles [22-25]. Plasma surface treatment is known to be an effective means of improving the dispersibility of minute particles of pigment.

In this study, we investigated plasma-assisted functionalization using radio frequency-plasma enhanced chemical vapor deposition (RF-PECVD), which uses a low pressure plasma. It can be applied to control the interaction between plasma and the ambient gas, and to observe the effect of plasma functionalization on electrospinning. Here, CB and P.R.48:2 pigments were treated with N_2 plasma to improve the extent of pigment dispersion in deionized (DI) water. The change in particle size was studied to elucidate the influence of N_2 plasma on the dispersibility of the samples. We also attempt to explain the dispersion mechanism of the N_2 plasma treatment in this paper.

Experimental Method

Materials

The CB (N220), whose primary particle size and specific surface area were approximately 20 nm and 120 m^2/g, respectively, used in this experiment was purchased from Sigma-Aldrich (USA). The P.R.48:2 (Azo 2B-Toner (Ca)) pigments, with 5.926 l/kg bulk volume and 59.1 m^2/g specific surface area, used in this experiment were provided by BASF (Germany).

Pretreatment process

The plasma surface treatment process for minute pigments (CB and P.R.48:2) was based on RF-PECVD. The details of the plasma setup are shown in Fig. 1. Initially, the dry powder cannot be placed directly in the vacuum chamber, because it will float. To prevent dust pollution and loss of pigments, 10 g of CB or P.R.48:2 powder was added to 10 ml of DI water, followed by sonication for 90 minutes to make a well-mixed solution. Then, the muddy solutions were drop-casted on a stainless-steel disc substrate with a diameter

of 10 cm. The samples were dried for 2 hours under ambient conditions to reduce the moisture content as much as possible.

Plasma treatment process

To treat the surfaces of the pigments, samples were placed on the base of the vacuum chamber of the RF-PECVD system (13.56 MHz), which was slowly evacuated up to 10^{-4} Torr. Then, N_2 gas (80 sccm) was purged to 10^{-2} Torr. During the experiments, the samples were exposed to the plasma, at a power of 300 W for 40 minutes.

Characterization

The morphologies and diameters of the CB and P.R.48:2 pigments were observed by scanning electron microscopy (SEM; S-4800; Hitachi, Japan) at an acceleration voltage of 15 kV. The samples were coated with Pt using an E-1010 ion sputterer (Hitachi) prior to characterization (20 mA, 10 Pa, 30 s).

Atomic force microscopy (AFM; XE-100; Park Systems, Korea) was used to investigate the three-dimensional (3D) morphologies and particle size distributions of CB and P.R.48:2 particles. The scanner was calibrated in both lateral and vertical directions with a standard grid. Typical measurement conditions were scan size of 3 μm and scan rate of 0.48 Hz.

The average particle size distributions of CB and P.R.48:2 pigments in DI water were measured by a laser particle sizer (AS-2012; AimSizer, China) with an extended submicron size range of 0.04-500 μm.

Fourier-transform infrared spectroscopy (FT-IR) of CB and P.R.48:2 pigments was carried out using an FT-IR 6300 instrument (JASCO, Japan) which was operated in transmission mode at room temperature in the range 550-4,000 cm^{-1}.

Results and Discussion

Fig. 1 shows the effects of the pretreatment and plasma treatment on the minute pigments (CB and P.R.48:2). To treat the pigments, we employed N_2 plasma with the RF-PECVD system. The pigments with or without N_2 plasma treatment were dispersed in DI water so that we could study their dispersibility. We initially compared the perceptibility of CB (0.0165 g) in DI water (35 ml) and P.R.48:2 (0.012 g) in DI water (15 ml) by observing ultrasonically vibrated (60 min) pigment solutions that had been left to stand for a fortnight (Fig. 2). The results clearly showed that, 2 weeks later, a precipitate formed in untreated CB pigment solution. However, in the case of the N_2 plasma-treated CB pigment solution, no such precipitate was observable by the naked eye. There was no obvious precipitate in either the untreated P.R.48:2 or the N_2 plasma-treated P.R.48:2 pigment solution. These differences were compared further in the experiments
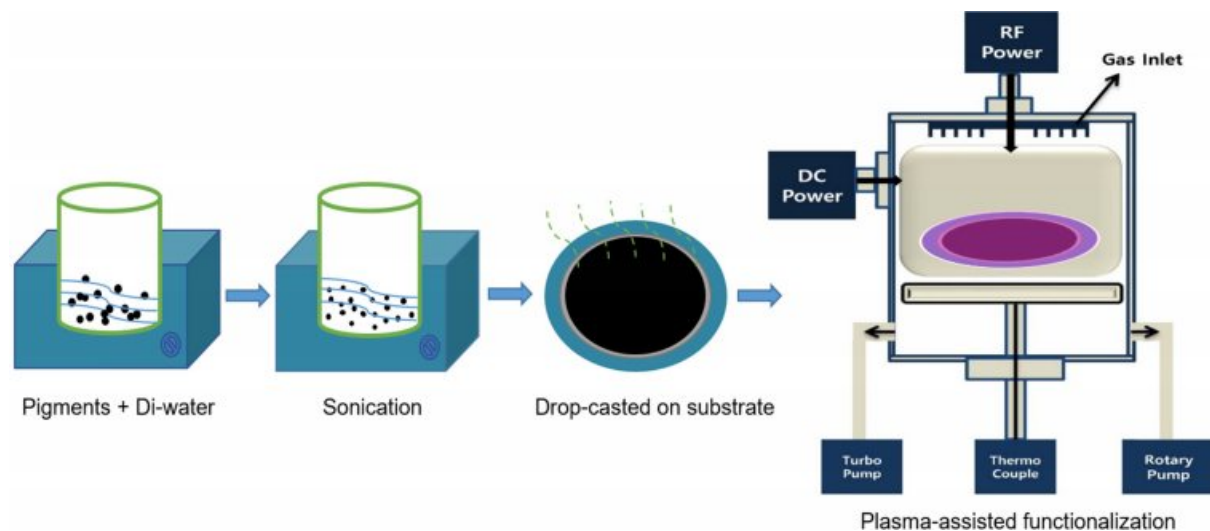
Fig. 1. Schematic of the N$_2$ plasma-assisted functionalization of pigments.
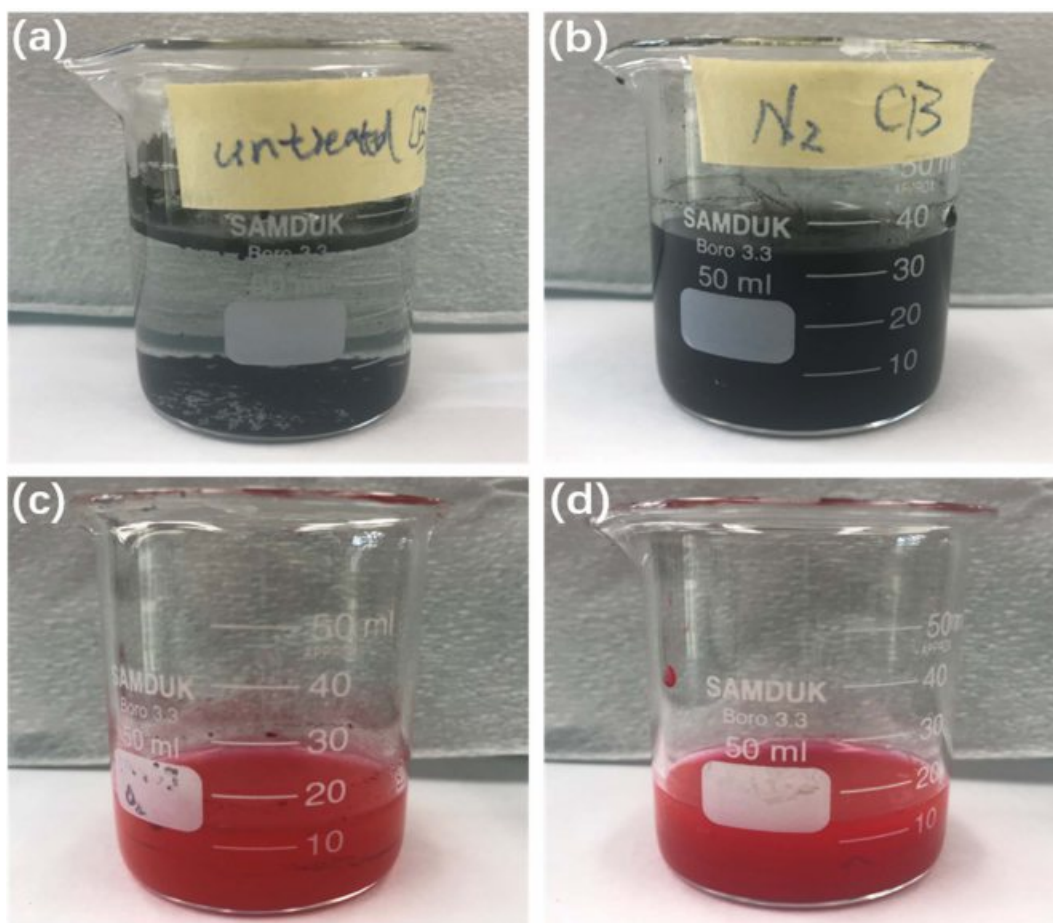

Fig. 2. Solutions of (a) untreated CB, (b) N$_2$ plasma-treated CB, (c) untreated P.R.48:2, and (c) N$_2$ plasma-treated P.R.48:2 respectively.

described in the following.

Firstly, morphologies and diameters of particles were characterized by SEM and AFM in order to investigate the differences in dispersion between untreated and N$_2$ plasma-treated pigments in DI water. Because the liquid samples cannot be observed directly, we first processed them by seeding particles on silicon wafers. The specific approach is as follows: (i) Small pieces of silicon wafer were cleaned for 5 minutes by ultrasonication in acetone, alcohol, and DI water; (ii)

the cleaned wafers were placed in untreated CB solution (Fig. 2(a)), N_2 plasma-treated CB solution (Fig. 2(b)), untreated P.R.48:2 solution (Fig. 2(c)) and N_2 plasma-treated P.R.48:2 solution (Fig. 2(d)); (iii) the solutions were undergone ultrasonic vibration for 30 minutes; (iv) then the wafers were removed from the solutions and dried in a vacuum drying oven at 60 °C for 12 hours. The SEM images (Fig. 3) and AFM 3D images (Fig. 4) show the morphologies of the particles on the wafers. Figs. 3(a) and (b) show SEM images of untreated CB and N_2 plasma-treated CB pigments. The results show that the N_2 plasma treatment was able to break down the agglomerates, and the particle size of CB pigments was reduced from 100 μmz to 500 nm. Figs. 3(c) and (d) show that N_2 plasma treatment can also help to break down agglomerates of P.R.48:2 particles; the P.R.48:2 particles were reduced from hundreds of micrometers to 20 μm. This illustrates that N_2 plasma treatment is an effective method for improving the dispersion properties of minute pigments in DI water. Figs. 4(a) to (d) show 3D images of untreated CB, N_2 plasma-treated CB, untreated P.R.48:2, and N_2 plasma-treated P.R.48:2 pigments, respectively. The results indicated many differences in morphology between the untreated particles and N_2 plasma-treated

particles. It is obvious that the particle size decreases after N_2 plasma treatment. Fig. 5 shows a region histogram plotted based on the AFM results. Figs. 5(a) and (b) show the particle size distributions (x axis direction) of untreated CB and N_2 plasma-treated CB pigments, respectively. Figs. 5(c) and (d) show the particle size distribution (x axis direction) of untreated P.R.48:2 and N_2 plasma-treated P.R.48:2 pigments, respectively. The region histograms show that, after N_2 plasma treatment, the particle distributions of both CB and P.R.48:2 pigments become narrow, and the particle sizes decrease. This further proves that N_2 plasma treatment is an effective method for improving the dispersion properties of minute pigments in DI water.

Secondly, for additional characterization of the dispersion properties of surface-modified pigments, a particle size analyzer was used to analyze the size distribution and average particle sizes of pigments in DI water. Before testing, the same concentrations of CB ultrasonicated solution and N_2 plasma-treated CB ultrasonicated solution were diluted 1,000 times. The same concentrations of P.R.48:2 and N_2 plasma-treated P.R.48:2 ultrasonicated solutions were also diluted 1,000 times. The diluted solutions were poured directly into quartz glassware for measurement. Fig. 6 shows
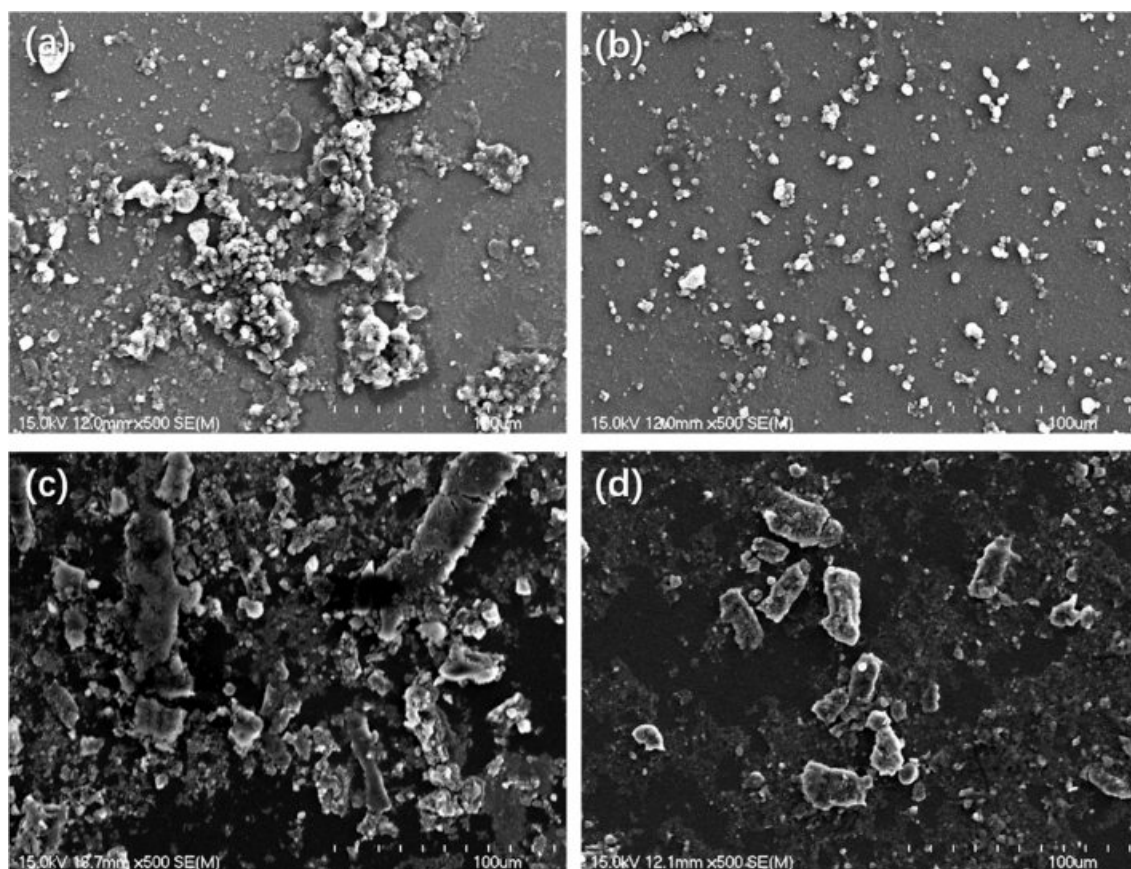

Fig. 3. Scanning electron microscopy (SEM) images of carbon black (CB) pigments (a) without and (b) with N_2 plasma treatment, and P.R.48:2 pigments (c) without and (d) with N_2 plasma treatment.
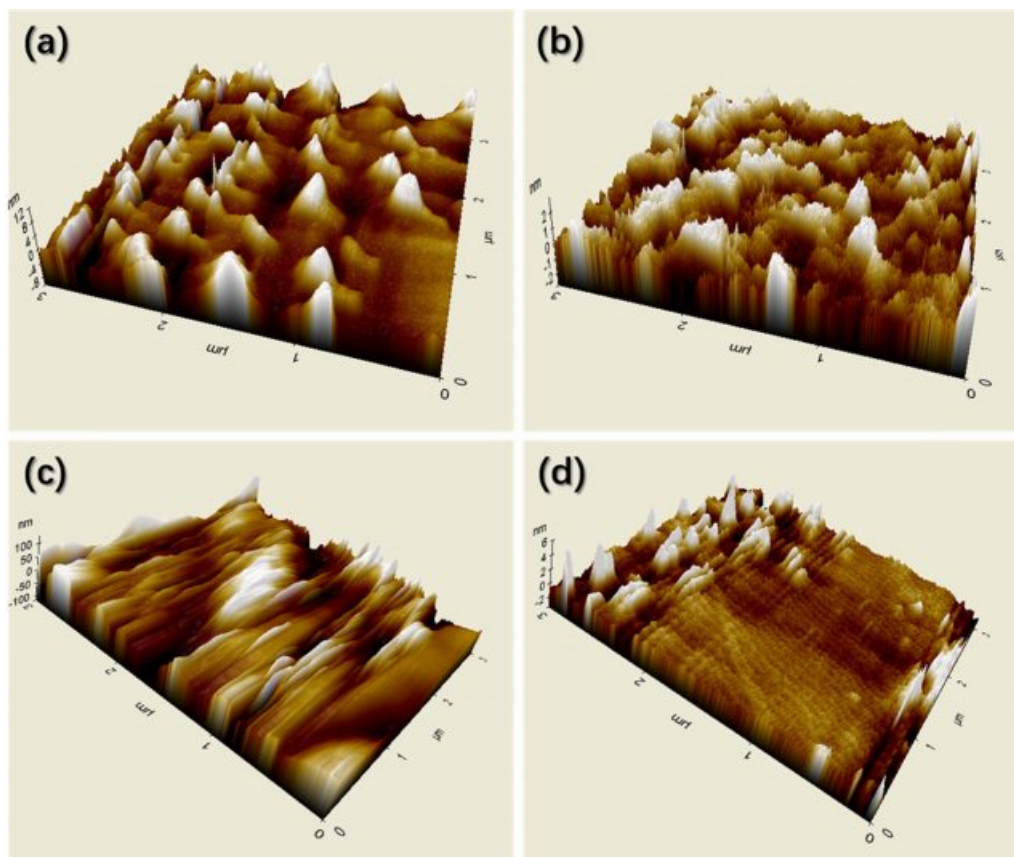
Fig. 4. Atomic force microscopy (AFM) images of CB pigments (a) without and (b) with N_2 plasma treatment, and P.R.48:2 pigments (c) without and (d) with N_2 plasma treatment.
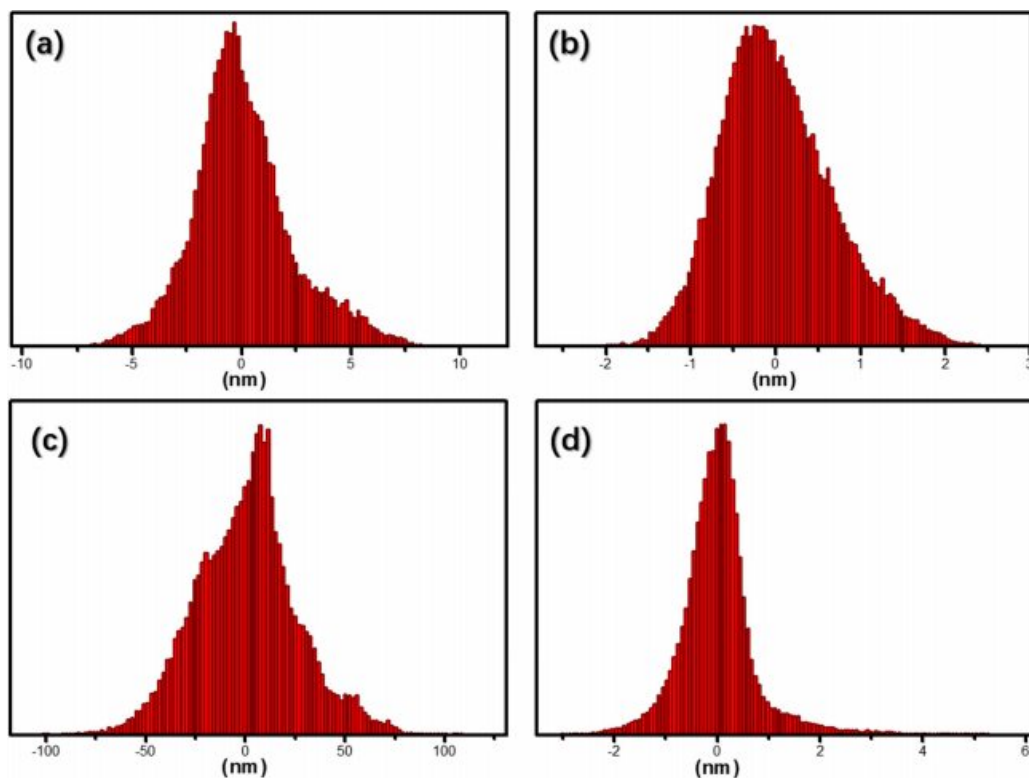

Fig. 5. The AFM particle size distribution of CB pigments (a) without and (b) with N_2 plasma treatment, and P.R.48:2 pigments (c) without and (d) with N_2 plasma treatment.

the particle size histograms of the CB and P.R.48:2 pigments. The results indicate that, after N_2 plasma treatment, the particle distributions of both CB and P.R.48:2 pigments narrowed. The average particle size of CB pigments decreased from 3,922 to 175.6 nm, and that of P.R.48:2 pigments decreased from 5,592 to 679.3 nm. These results are consistent with the SEM and AFM results. Explanation for particle size reduction for both CB and P.R.48:2 pigments are different. For CB, improvement of London dispersive component of the surface free energy and surface functional groups after plasma treatment result in particle size is decreased and dispersibility in DI water is increased, respectively [26]. For P.R.48:2, polymer chain cleavage and/or cross-linking reactions are expected during plasma

treatment [27]. Although such reactions cannot be documented in aforementioned analyses, data pointed out that exposure of plasma treatment of all the samples yield cleavage reactions rather than cross-linking, which result in smaller particle size.

Thirdly, FT-IR characterization was performed to investigate the types and extent of changes in functional groups on the surfaces of the particles after N_2 plasma treatment, and the results are shown in Fig. 7. By comparing the changes in the peaks of the CB particles after N_2 plasma treatment (Fig. 7(a)), we investigated the effect of N_2 plasma treatment on CB pigments. We can see from Fig. 7(a) that peaks at 1,526, 1,706, 2,890, 2,960, 3,333, 3,619, 3,742, and 3,835 cm^{-1} are present in all samples, without obvious differences. These are
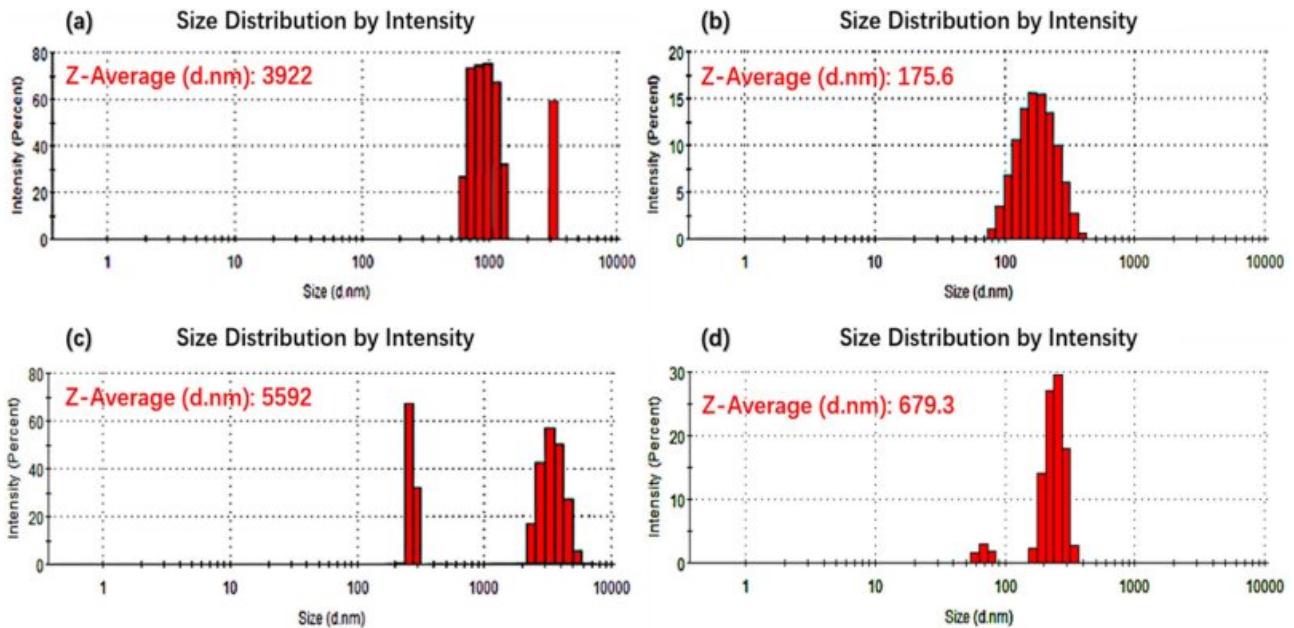

Fig. 6. Particle size histogram of CB pigments (a) without and (b) with N_2 plasma treatment, and P.R.48:2 pigments (c) without and (d) with N_2 plasma treatment.
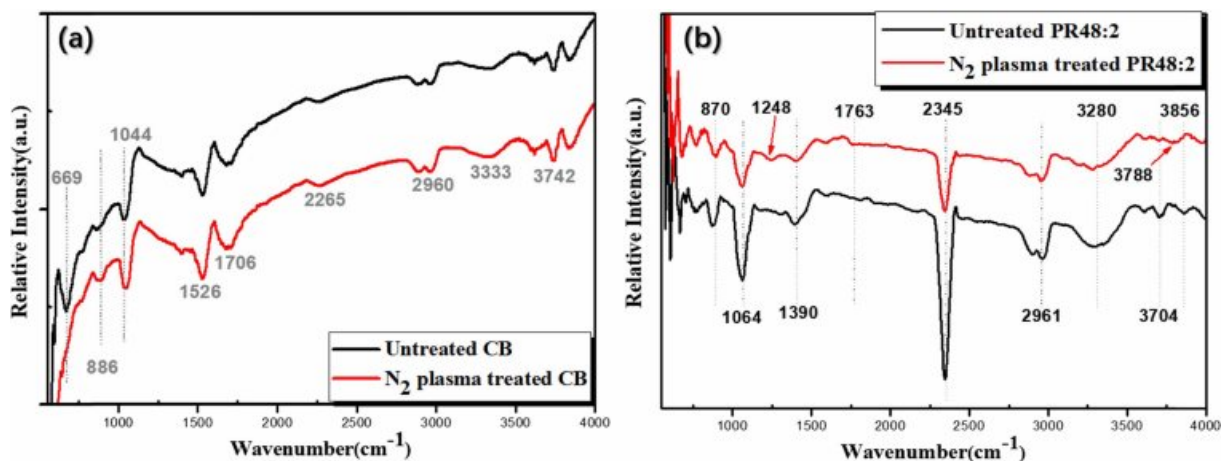

Fig. 7. Fourier transform-infrared (FT-IR) spectra of PVDF-HFP, CBs/PVDF-HFP, CBs-O_2/PVDF-HFP, and CBs-N_2/PVDF-HFP electrospun composite fiber films, and CBs, CBs-O_2, and CBs-N_2 powders.
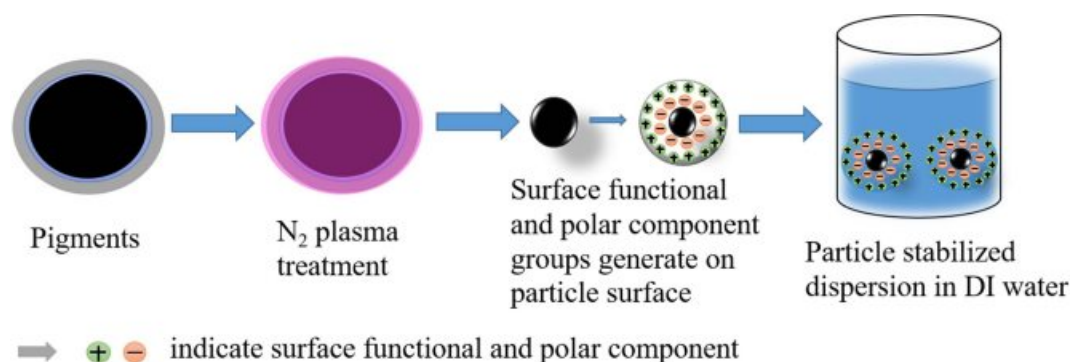
Fig. 8. The mechanism of the N$_2$ plasma-assisted functionalized pigment dispersion process in deionized (DI) water.

assigned to carboxyl C or aromatic C, ketone, C-H asymmetric stretch, methylene band, hydroxyl group, non-bonded hydroxyl group, and broad water band, respectively [28-30]. However, the peak of untreated CB pigments at 669 cm^{-1}, which can be linked to a specific vibration as the stretching between carbon and hydrogen (out-of-plane C-H bend) [29], disappeared after N$_2$ plasma treatment. Furthermore, the peaks at 886 cm^{-1} (hydrogen-bonded O-H out-of-plane bending) [29] and 1,044 cm^{-1} (C-O stretching) [31] increased after N$_2$ plasma treatment. This suggests that out-of-plane C-H bonds of CB were broken by the N$_2$ plasma treatment, where these broken bonds would generate oxygen-containing groups, such as O-H and C-O groups, in the atmosphere [32]. We also compared the FT-IR curves of untreated P.R.48:2 and N$_2$ plasma-treated P.R.48:2 particles. The FT-IR spectra of untreated P.R.48:2 pigments contained prominent peaks at 762, 870, 1,064, 1,390, 1,588, 2,345, 2,898, 2,961, 3,280, 3,613, 3,704, and 3,856 cm^{-1}, as shown in Fig. 7(b). The bands at 762 cm^{-1} and 870 cm^{-1} are due to aromatic C-H and epoxy ring vibration. The C-O stretching of alkyl-substituted ether and C-N stretching appears at 1,064 cm^{-1}. The carboxylate stretching is situated at 1,390 cm^{-1}. The bending at 1,588 cm^{-1} corresponds to open-chain azo vibration. The peak at 2,345 cm^{-1} corresponds to nitrile group stretching. The P.R.48:2 spectra also show absorption bands derived from the C-H stretching vibration in CH$_x$ functional groups, at approximately 2,898 and 2,961 cm^{-1}. The peaks from 3,280 to 3,856 cm^{-1} correspond to hydroxyl stretching [29, 33]. However, after N$_2$ plasma treatment, all the characteristic peaks of the original P.R.48:2 decreased and new peaks appeared at 1,248 cm^{-1} (aryl-O stretch) and 1,763 cm^{-1} (open-chain acid anhydride). Furthermore, the hydroxyl bending at 3,613 and 3,704 cm^{-1} shifted to 3,788 cm^{-1} [29]. We believe that this is because the N$_2$ plasma treatment affected the bond vibrations of P.R.48:2, and oxygen-containing groups (aryl-O stretching, open-chain acid anhydride and hydroxyl) were generated on the surfaces of the P.R.48:2 particles.

Lastly, based on the results of our FT-IR analysis and other studies, we propose a mechanism as shown in Fig. 8, in which N$_2$ plasma treatment may affect the dispersion of minute pigments in DI water. N$_2$ plasma treatment is expected to improve both the stable micro-structure and surface functional groups of nanostructured particle surfaces, which are correlated with the London dispersive component and the specific (or polar) component including electron acceptors and donors of the surface free energy, respectively [26]. These will help to decrease the sizes of the particles and increase their wettability [34, 35]. As a result, improve the particle dispersion, prevent the particles agglomeration, and remain stabilized in DI water [36].

Conclusion

In summary, we investigated the effects of N$_2$ plasma treatment on the dispersion properties of pigments with minute particle sizes (CB and P.R.48:2) in DI water. To study the dispersion properties of CB and P.R.48:2 pigments, we carried out many types of analysis, such as SEM, AFM, particle size tests, and FT-IR. Based on all of our analytical results, we reached the following conclusions: 1. The SEM, AFM, and particle size test results showed that N$_2$ plasma treatment effectively reduces the particle sizes of the minute pigments, and narrows the particle size distribution of both CB and P.R.48:2 pigments; 2. The FT-IR analysis helped us to characterize the functional groups on the surfaces of pigment particles after N$_2$ plasma treatment, and the results suggest that the number of functional groups on the surfaces of the pigment particles increased; 3. Based on our analysis results, and intensive research, we proposed a mechanism by which the N$_2$ plasma treatment may affect the dispersion of minute pigments in DI water; namely, N$_2$ plasma treatment may provide functional groups, including a London dispersive component and a specific (or polar) component, with electron acceptor and electron donors, respectively, of the surface free energy. This helps to decrease the particle size and increases their wettability. Therefore, after N$_2$ plasma treatment, the particle sizes of the

pigments decreased and dispersed steadily in DI water.

Acknowledgments

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