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Visualization and Quantitation Technology of Carbon Black Dispersion State in Intermediate Transfer Belt Using Confocal Laser Scanning Microscope

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Abstract

The intermediate transfer belt for electrophotography is an important component which affects the image quality. To express the transfer function of the belt, it is required to stably control its electrical characteristics. Conventionally, it has been difficult to observe the state of the Carbon Black (CB) dispersed all over the cross-section of the intermediate transfer belt with a wide field of view using an electron microscope while keeping high resolution. This time, therefore, as a new technology for observation, we have introduced confocal fluorescence microscope which is used for biological sample observation and succeeded in observing the CB dispersion state in Poly Vinylidene di Fluoride (PVDF) as a scattered image. Based on this image we quantified the CB dispersion state using the quadrat method and as a result, we confirmed a good correlation in the electric characteristics of the belt. In this report, we will confirm the effectiveness of the new technology for observation and quantitation to visualize the CB dispersion state in the composition where electro conductive CB has been dispersed in PVDF. Furthermore, we will discuss the relation between the quantified CB dispersion state and the electric characteristics of the belt.

Introduction

Recently there has been a growing trend toward the protection of the environment. In line with this, the manufacturer has been required to promote design and development activities taking CO_2 emissions, energy consumption, chemical usage and others into consideration in the manufacturing process of the product. Environment-friendly product development is required even in the component development of electrophotography which is an imaging system of copying machines and printers for business and family use. At the same time it is also required to realize high performance equivalent to or higher than that of conventional components.

The transfer system of electrophotography is a two-stage transfer system where the toner image formed on the photoreceptor is transferred to the intermediate transfer belt and then it is overlapped on the intermediate transfer belt (first transfer) and finally it is transferred to paper (second transfer) (Fig.1). The intermediate transfer belt is required to have mechanical characteristics of durability and electrical characteristics of stable semi-conduction to obtain high image quality.

To meet these requirements, thermosetting resin (PI, PAI and others) has been used as a base material of intermediate transfer belt. The thermosetting resin belt is produced using a centrifugal molding method. In this method, the intermediate transfer belt is produced by uniformly dispersing resin material, conductive material of carbon black (CB) and other additives in the organic solvent, applying them to the cylindrical mold and performing the process of drying, firing and end part treatment while rotating the mold. There are two problems; (1) the thermosetting resin belt requires a large amount of organic solvent in the production process and (2) high load is imposed on the environment due to one by one production. [1]

To solve these problems, a thermoplastic resign based intermediate transfer belt has been developed, which can be produced without using organic solvent. We selected fire resistant thermoplastic resin PVDF as a base material in developing the intermediate transfer belt. The thermoplastic belt is produced in the following sequence based on continuous extrusion molding. First of all, resin material, CB and additives are melt/kneaded and cooled by using a biaxial extruder to create a pellet. The pellet is again melt/kneaded using an extruder, put in the cylindrical mold, cooled with inner sizing, and formed a desired size.

The electric characteristics of the thermoplastic belt can be adjusted by controlling material melting/kneading conditions in the production process (temperature, velocity, number of kneading and others) and mold conditions (temperature of mold, cooling velocity and others). This method allows continuous production of intermediate transfer belt without using solvent and solves the problem associated with the thermosetting resin belt. However, the control of the condensed state of CB (conductive path) inside the intermediate transfer belt is difficult compared to that of the thermosetting resin which disperses the CB using organic solvent. Thus, it is difficult to obtain homogeneous intermediate transfer belt without in-plane variations in the electric characteristics.

Therefore, it is important to visualize the dispersion state of the CB inside the resin and clarify the relation with the electric characteristics of the intermediate transfer belt prior to developing the thermoplastic resin belt. The CB dispersed in the resin exists in the state where approx.100 to 500nm condensed aggregate structure made up of single particles with a diameter of 30 to 50nm (primary aggregates) and 10 to 100µm further condensed agglomerates (secondary aggregates) are mixed. Currently, electron microscope is used as a method to observe them. [2][3]

However, since the resin molded as intermediate transfer belt has several hundred µm of thickness, it was difficult to obtain information directly linked to the electric characteristics of intermediate transfer belt only by partial observation of the dispersion state of CB aggregates having several hundred nm. Furthermore, observing the state of the CB dispersed all over the cross-section of the intermediate transfer belt using an electron microscope requires taking several tens of pictures and joining them. This was not a practical method.

Therefore, regarding the developed PVDF intermediate transfer belt, this study aims to visualize and quantify the state of the CB dispersed all over the cross-section of the belt having several hundred μm thickness and discuss the relationship with the electric characteristics of the belt. As a method for this, we will consider the method using confocal fluorescence microscope which is equipped with weak scattered light detector and multi-wavelength excitation laser and used for biological sample observation. Furthermore, we will discuss the state of the CB dispersed all over the cross-section of the belt which has been observed using this method and the relationship with the electric characteristics of the belt.

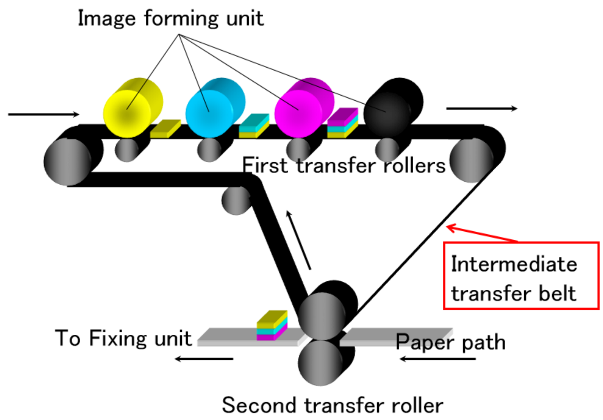

Figure 1. Schematic diagram of intermediate transfer

Experiment

Procedure for extrusion molding of PVDF intermediate transfer belt

We premixed PVDF and CB, and melt-kneaded them using a twin screw extruder. We then cooled the kneaded material for pelletizing. Before injecting the pellet into the belt molding device, we put it in the hot-air-drying area at a temperature of 80 degrees for 6 hours (Fig.2). We finally injected the pellet into the belt molding device as shown in Fig.3 for melt-kneading and put it in the cylindrical mold, cooled with inner sizing, and formed a desired size

The surface resistance value of the belt was controlled by adjusting the mold temperature and the number of material kneading times. As shown in Table.1, we created 4 samples (1)-4)) which have a different surface resistance value respectively.

The mold temperature and the surface resistance value of the belt were measured at 500V applied voltage with URS probe using Mitsubishi Chemical Hiresta UP.

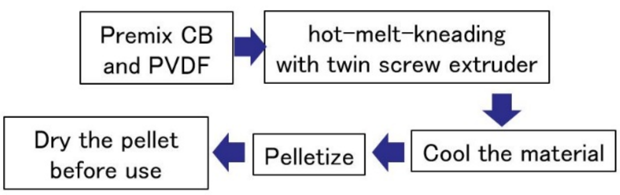

Figure 2. Production Process of the raw material of the "intermediate transfer belt".

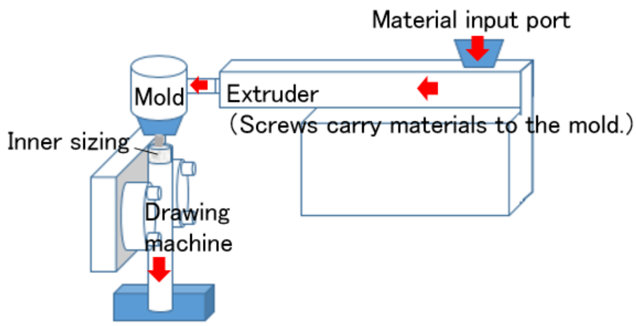

Figure 3. Schematic diagram of belt production machine

Table 1. Mold temperature, number of material kneading and surface resistivity (ρS500V) of the produced belt of molding device

Sample No.	Mold temperature	Material kneading number of times	logρS500V
1)	180°C	1 time	11.52 (Ω/□)
2)	195°C	1 time	11.23 (Ω/□)
3)	200°C	1 time	10.75 (Ω/□)
4)	180°C	2 times	10.66 (Ω/□)

Procedure of observation with a microscope

According to Abbe's rule, the size of a structure that can be observed with an optical microscope is up to half of that of light wavelength. In this study, however, we target a structure smaller than it. Therefore, to observe the state of dispersion of a several ten to several hundred nm CB aggregate, we targeted a scattered image for this observation. [4]

We used a refractive index matching (RIM) technique which uses oil immersion lens to observe the weak scattering light in high resolution among laser light entering the CB inside the resin. As the performance of objective lens, if the medium is dry objective lens of air (refractive index: n=1), the value of numerical aperture (NA) that determines an important resolving power along with magnification never exceeds 1 at most. However, if liquid-immersed objective lens is used that fills space between objective lens and cover glass with the liquid having almost equal refractive index, the light comes in the objective lens with almost no reflection at the interface between cover glass and oil. Thus, NA can be set to 1.0 or higher, which enables observation in higher resolution.

In addition, using Immersion Oil (n=1.52) having a refractive index almost equal to that of PVDF (n=1.43) enables the observation in high resolution with reduced aberration when obtaining the scattering image of the CB. It also enables the extrusion of CB images only since the refractive index is matched and the PVDF resin binding the CB becomes transparent. Furthermore, using Leica SP8 biological fluorescence microscopy enables the capturing of weak scattering light and the wide area scanning with less distortion.

Observation and analysis procedure

From each sample of PVDF intermediate transfer belt (1)-4)) we produced thin test pieces having thickness of 90nm that is less than that of an optical slice thickness of the fluorescence microscope by using the ultra-microtome. We then pasted the produced thin test pieces on the cover glass subjected to a hydrophilic treatment and observed them using a Leica TCS SP8 STED CW with 100 times, NA=1.40 oil immersion lens (HCX PLAPO). We captured a scattering transmission image in 633nm laser wavelength, 155 x 38μm image area, 1024 x 256 pixel image and 8-bit (256 gradations).

To visualize the dispersion state of the CB in the image, we divided the image of 38μm square on the surface side of the captured cross sectional image of the belt into small partitions of 3μm square using analysis software (Quadrat Method).[5] We calculated the level of 256-gradations for each small partition and the standard deviation of the square root of the variance from the gradation value of all internal partitions, and created a histogram of the CB dispersion state.

Results

The state of the CB dispersed all over the cross-section of the intermediate transfer belt in the depth direction was obtained as a scattered image (Fig. 4). The CB dispersion state all over the cross-section of the belt could altogether be observed at high resolution, which has conventionally been impossible. The portion where the CB exists appears black and the portion of the PVDF base material appears white. Since this image is a scattered image, the actual size of the CB aggregate is not that appears on the screen. It depends on the image luminance (density) that is captured in 8-bit/256 gradation.

A histogram of the CB dispersion state was formed from an image luminance (Fig.5). Conditions of the temperatures when forming the belt were controlled to form a sample having a different resistivity (Table.1). In addition, Fig.6 shows a luminance histogram of small partitions which was calculated from the cross-sectional CB dispersion state image of the belt samples having different mold conditions (1)-4)) and surface resistivity. From this result and the surface resistivity of each sample shown in Table.1, it is known that those samples having higher surface resistivity generate peak values in the right side of the histogram and those having lower surface resistivity generate peak values in the left side of the histogram. This means that the standard deviation of gradation is large. In other words, those belts showing inhomogeneous CB dispersion state tend to have higher resistivity and those showing homogeneous CB dispersion state tend to have lower resistivity.

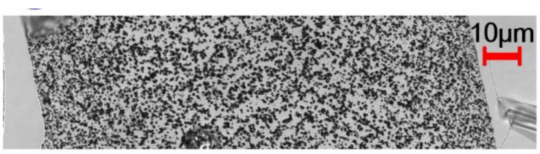

Figure 4. Scattered image of a cross-section of intermediate transfer belt.

The result obtained by observing the thin test sample of the cross-sectional intermediate transfer belt at laser wavelength of 633nm using the oil immersion lens. The portion where the CB exists appears black and the portion of the PVDF base material appears white. Since this image is a scattered image, the actual size of the CB aggregate is not that appears on the screen. It depends on the image luminance (density) that is captured in 8-bit/256 gradation.

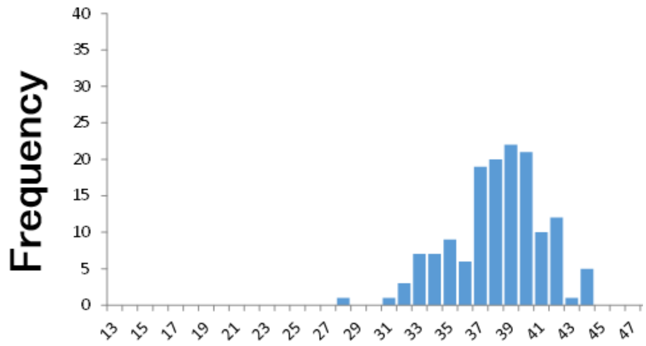

Figure 5. The histogram obtained by dividing the image of 38μm square on the surface side of the cross-sectional image of the belt into small partitions of 3μm square using Quadrat Method (Fig.4) and calculating the level of 256-gradations for each small partition and the standard deviation.

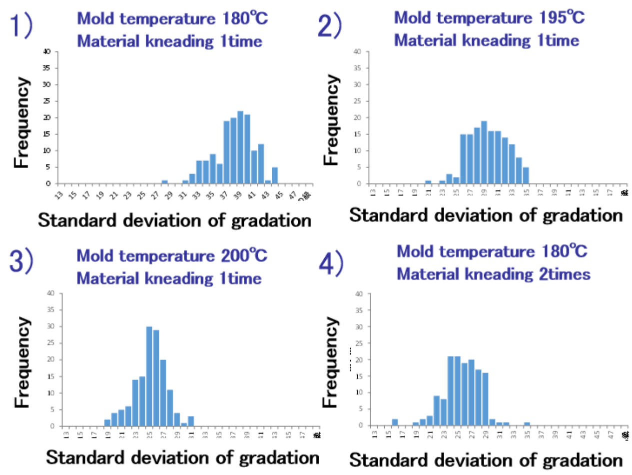

Figure 6. The histogram of each belts having different resistivity.

The histogram obtained by dividing each cross-sectional image of the belt having different resistivity into small partitions of 3μm square using Quadrat Method and calculating the level of 256-gradations for each small partition and the standard deviation. Numerals of each figure are the number of the sample shown in Table 1.

Discussion

From the above result, we considered the relation between the belt mold conditions (mold temperature and number of material kneading) shown in Table.1 and the surface resistivity of the produced intermediate transfer belt and the relation between the histograms of each sample shown in Fig.6.

First, we compared the test result corresponding to Sample Nos. 1), 2) and 3). As shown in Table.1, it was conventionally known that the intermediate transfer belt produced at higher mold temperature has a decreased surface resistivity. We then observed the state of the CB dispersed all over the cross-section of the newly obtained belt and created a histogram of standard deviation of the dispersion state using Quadrat Method (Fig.6). As a result, it has been known that the samples produced at higher temperature tend to show more homogeneous CB dispersion state of the cross-section of the intermediate transfer belt.

Similarly, we compared the test result corresponding to Sample Nos. 1) and 4). It was conventionally known that the intermediate transfer belt produced at a larger number of material kneading has a decreased surface resistivity. We then observed the state of the CB dispersed all over the cross-section of the newly obtained belt and created a histogram of standard deviation of the dispersion state using Quadrat

Method (Fig.6). As a result, it has been known that the samples produced at a larger number of material kneading tend to show more homogeneous CB dispersion state.

In other words, mold temperature and number of material kneading are the energy necessary for the CB being dispersed homogeneously in the resin. In the intermediate transfer belt which was produced under the condition of larger energy being applied, since the CB was dispersed homogeneously in the resin, conductive path was formed, leading to a better current flow and lower resistivity (Fig.7(a)). On the other hand, in the intermediate transfer belt which was molded under the condition of lower mold temperature or less number of material kneading (sufficient amount of energy is not supplied which is necessary for the CB being dispersed homogeneously), since the CB was not dispersed homogeneously, it was assumed that conductive path was not formed appropriately, leading to an insufficient current flow and higher resistivity (Fig.7(b)).[6]

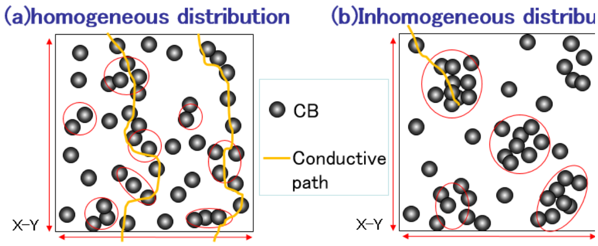

Figure 7. Schematic diagrams in consideration of relation between the CB dispersion state and the surface resistivity in the cross-section of the PVDF intermediate transfer belt

Conclusion

We have developed a new technology for visualizing and quantitating dispersion state of carbon black in PVDF by using laser scanning fluorescence microscopy featuring confocal optics and clarified relation between the resistivity and the CB dispersion state of the cross-section of the belt. We confirmed the technology is capable of observing a wide field while keeping high resolution. We will further verify whether this method is also applicable to fillers other than CB and resins other than PVDF for similar observation and evaluation of the dispersion state.

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Author Biography

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