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Study on correlation of filtration performance and charge behavior and crystalline structure for melt-blown polypropylene electret fabrics

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ABSTRACT: Melt-blown polypropylene (PP) electret fabrics are widely used as air filter media due to the specific mechanism of electrostatic filtering. In this article, two additives, stearate and modified rosin, are doped to PP fabrics during melt-blown process. The filtration performance of doped PP gets improved greatly, with filtration efficiency increased by 6% at room temperature but its temperature stability promoted dramatically. As a result, the filtration efficiency of doped PP still remains above 95% of its initial, whereas that of non-doped PP only remains 58% at 110°C. By XRD characterization the structure modification is observed after doping. The crystallinity increases from 14.17% to 22.64% and 29.62%, respectively. Meanwhile, the crystallite has a smaller size, respectively, 89Å and 86Å as compared to 107Å for non-doping in the direction vertical to lattice plane (110). This demonstrates that additive doping can give rise to larger crystallinity and more fine-grained crystallite. Therefore, doped PP improves its charge storage behavior ascribing to expanding interface between crystallite and amorphous region and then enlarging charge trap density. Furthermore, the effect of additive doping on electret charge storage behavior is investigated by short-circuit TSD, and the filtration performance can be explained relevantly with TSD. A charge storage profile is also adopted to illustrate that the space charge captured by charge traps is in the form of space-charge dipole with the rigidity of crystallite. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42807.

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INTRODUCTION

Because of unique electrostatic filtering mechanism, melt-blown polypropylene (PP) electret fabrics are more widely used as air filter media in contrast with non-electret fabrics only with mechanical mechanism including inertial capture, interception and diffusion.[1,2] It is considered as the best portable air purification material applied currently in residential environment especially in reducing indoor exposure to influenza particles.[3] Its outstanding filtration performance mainly depends on the superior electret charge behavior.[4] How to improve its charge storage behavior and then to enhance its filtration performance has always been challenging.

As is well-known, the charge storage capacity of electret is related to charge traps which prohibit or restrain charge drift through surface and/or bulk, and the morphology and impurities play an important role on electret features consequently.[5,6] As being semi-crystalline polymer for PP, the density and nature of its charge trap are expected to have connection with the crystalline features such as amorphous-to-crystalline boundaries, surface morphology, and impurities.[7,8] Among a lot of methods proposed to improve PP's crystallite features, additive doping is effective. For example, Thyssen *et al.* explored the influence of nucleating agents with different concentrations on the morphology of biaxially stretched PP-film and its electret feature as well. They pointed out that electret charge stability is related to the spherulites of PP and smaller spherulites results in more stable electrets.[9] Mohmeyer *et al.* observed that the addition of tripheylamide derivatives as nucleating agents at optimal concentration may influence the charge storage property of PP film and the formation of isolated nanometer-sized supramolecular structure is important for the improvement of electret feature.[10] Behrendt *et al.*, researched the impact of crystal modification with α and β nucleating agents on the electret property of PP film, and no significant difference was observed for α and β nucleated specimens.[11] Hillenbrand *et al.* reported that biaxially stretched PP electret film with additives including $CaCO_3$ and Al_2O_3 has better charge stability than pure PP.[12]

The aim of this research is to explore the impact of additives on charge storage behavior of melt-blown PP electret fabrics. The effect of additive doping on filtration performance is investigated and the crystalline structure of PP fabrics is measured

by means of XRD. The correlation between filtration performance and crystalline structure is discussed. The mechanism for enhancing charge storage capacity and consequently improving filtration performance is proposed.

EXPERIMENTAL

Materials

Melt-blown PP fabrics with the basic weight of 40 g/m^2 are produced in the melt-blown installation by Zhejiang Zhaohui Filter Technology (China). Granule PP with melting index of 1200 from Shandong Dawn Polymer (China) is homogeneously blended with additive (0.5 wt %, optimal concentration for melt-blown PP processing) in a three-dimensional motion mixer beforehand. Two kinds of additive, stearate and modified rosin, are commercially available.

Three samples, abbreviated as P0 (pure PP fabrics), P1 (modified rosin doped), and P2 (stearate doped), are prepared. Testing sample is cut into 15 cm × 15 cm from the same batch. The electret of PP fabrics is formed via a corona charging system with adjustable electric field applied by high-voltage power source.[13]

Measurement of Filtration Efficiency

Filtration efficiency is measured with an automated filter tester made by Zhejiang Zhaohui Filter Technology (China). The measurement area is 50 cm^2. Generated from a collision nebulizer, KCl is used as challenge aerosol with flow rate of 5.3 cm/s. A Kr85 sealed source is employed to neutralize the aerosol charge to a Boltzmann charge distribution. The concentrations of challenge aerosol in the upstream (Cu) and downstream (Cd) are respectively measured with a wide range particle spectrometer. Filtration efficiency η is calculated as follows: $\eta = (1 - Cd/Cu) \times 100\%$. Aerosol particle size for measurement is in the range of 0.3–0.5 μm.

To investigate the stability of filtration efficiency under ambient storage, as-prepared samples are stored in a thermostat with constant temperature of 25°C and humidity of 50%. The η value is the average of three parallel samples. To test the temperature stability of filtration efficiency, the sample is first put in an oven with constant temperature for half an hour, and then taken out to perform the measurement immediately.

Crystal Structure Characterization

It is well-known that the crystalline feature can affect the property of semi-crystalline polymer. The X-ray diffraction (XRD) measurement is applied to study PP fabrics crystalline structure in this article. Crystal phase composition and crystallinity are detected by the X-ray diffraction meter from Philips, Netherlands (X pert MPD Philips) with Cu $K\alpha$ irradiation. It is operated at a power of 40 kV × 45 mA under ambient temperature. Radial scans versus diffraction angle are carried out in the range of 10–40° with scanning rate of 1°/min and step size of 0.02°. The inner planar distance d is calculated by the Bragg equation $d = \lambda/(2\sin\theta)$, in which λ ($\lambda = 0.154056$ nm) is the radiation wavelength, θ is the Bragg angle. Lamellar size L_{hkl}, in the direction vertical to the lattice plane (hkl), is calculated by Scherrer formula $L_{hkl} = k\lambda/(B\cos\theta)$, where k ($k = 0.9$) is the structure factor, B is the full-width at half-maximum of the (hkl) diffraction peak.

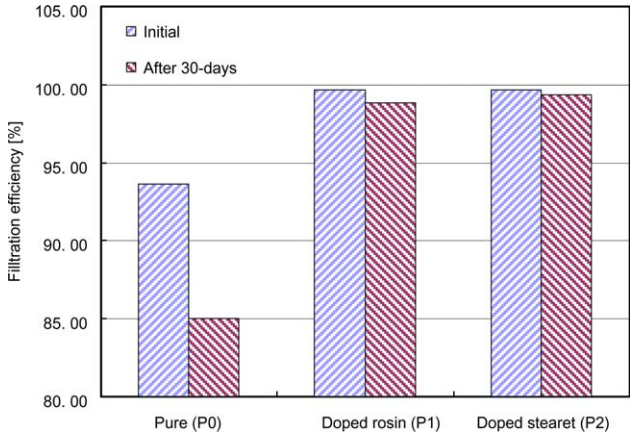

Figure 1. Filtration efficiency of melt-blown PP electret fabrics before and after stored at room temperature for 30 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Test of Thermally Stimulated Discharge Current

To reveal the electret charge storage behavior of melt-blown PP electret fabrics, the measurement of short-circuit thermally stimulated discharge (TSD) current spectra is carried out using custom-designed apparatus with temperature-programming controlled oven. The induced current by the sample through electrode is recorded in situ by an electrometer (Keithley 6517). The test area is 3 × 3 cm^2. The heating rate is 3°C/min for TSD current spectra measurement.

RESULTS AND DISCUSSION

Effect of Additives on Filtration Performance

A control experiment for filtration efficiency (η) stability is carried out. The as-prepared samples are measured before and after stored for 30 days under room temperature. The results are shown in Figure 1. The initial η (before storage) for doped samples (P1 and P2) gets an obvious enhancement versus that of non-doped sample (P0). The initial η for sample P0 was 93.62%, wherreas samples P1 and P2 increased to 99.43% and 99.68%, respectively. After stored for 30 days, the initial η for sample P0 descended to 85.01% by 8.61%, whereas samples P1 and P2 descended to 98.83% and 99.37% only by 0.86% and 0.32%, respectively. It illustrates that additive doping can enhance filtration efficiency. After doping, not only does the initial η increases, but η stability under ambient storage also gets improved dramatically (Figure 1).

Additive doping can also improve the temperature stability of filtration efficiency. A test of thermally stimulated filtration efficiency decay is carried out. The results are plotted in Figure 2. The η value for samples P1 and P2 hardly descends when the temperature rises from 25°C to 70°C, and decreases only a little at elevated temperature. Even when the temperature increases to 110°C, the η value for samples P1 and P2 still keeps more than 95% of its initial. However, the η value for sample P0 starts to decline gradually and decay rapidly after 70°C, resulting in 58% of its initial at 110°C. As a result, additive doping can also

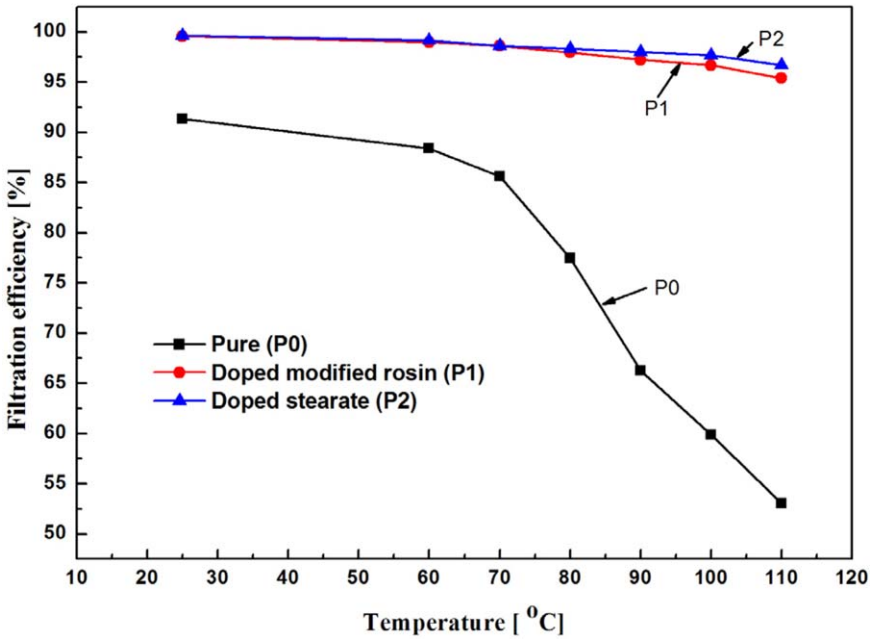

Figure 2. Filtration efficiency of melt-blown PP electret fabrics as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improve the temperature stability of filtration efficiency for melt-blown PP electret fabrics dramatically. It is concluded that filtration performance gets improved greatly by doping.

Effect of Additives on Crystalline Structure

The XRD patterns for samples P0, P1, and P2 are displayed in Figure 3. As reported in literatures,[14,15] five diffraction peaks in every single curve correspond to the lattice planes (110), (040), (130), (111), and (041), respectively, which are all characteristic of α phase with monoclinic configuration for PP. It can be figured out that the diffraction peak 2θ are in good agreement with reference[16] but the relative intensity of diffraction peak in this study differentiates from that in reference.[11] The relative intensity for lattice plane (111) is significantly reduced and its diffraction peak overlaps with that of (041), which can be attributed to the melt-blown processing for PP fabrics. The same characteristics for relative diffraction intensity for every lattice plane are observed for melt-blown PP fabrics from different sources. No evidence of β phase is observed on the condition of melt-blown crystallization for PP fabrics.[17] It is confirmed that melt-blown PP fabric predominately crystallizes into α phase.

A series of crystal parameters calculated from XRD patterns of Figure 3 are exhibited in Table I. Crystallinity percentage is obtained by Hinrichsen's method.[11,18] The crystallinity is 14.17% for sample P0 and increases to 22.64% and 29.62% for samples P1 and P2, respectively. The above results imply that additive doping can improve the crystallinity of melt-blown PP fabrics. Also seen from Table I, crystallinity is related to the property of additive. The nucleation effect of stearate is better than that of modified rosin at 0.5 wt % doping concentration.

From Table I, the Lamellar size L_{hkl} of doped PP fabrics is a little smaller than that of pure PP fabrics, indicating the formation of more "fine-grained" morphology. For example, L_{110} for pure PP fabrics is 107Å. While after doping modified rosin and stearate, L_{110} decreases to 89 Å and 86 Å, respectively. It hints that additive molecule becomes the nucleating center and induces epitaxial growth of α-crystal, which leads to the reduction of its crystallite size and the increase of its crystallinity.

The effect of additives on the crystalline structure of PP has been extensively investigated by many researchers.[19,20] It is well-known that modified rosin is typically a nucleation agent inducing the α-modification for PP at a low concentration.[21] As ester,

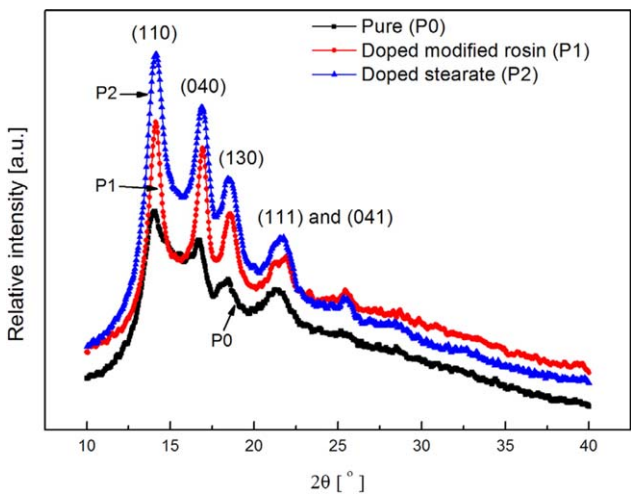

Figure 3. XRD diffraction pattern of melt-blown PP electret fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Crystal Parameters of Melt-blown PP Electret Fabrics Calculated from XRD Patterns

Sample fabrics	Crystal plane (*hkl*)	$I_{(hkl)}/I_{(110)}$	2θ(deg.)	d(Å)	L_{hkl}(Å)	Crystallinity (%)
P0	(110)	1.00	14.040	6.334	107	14.17
	(040)	0.48	16.720	5.265	145	
	(130)	0.30	18.440	4.234	115	
P1	(110)	1.00	14.000	6.339	89	22.64
	(040)	0.45	16.800	5.267	130	
	(130)	0.27	18.440	4.818	107	
P2	(110)	1.00	14.160	6.319	86	29.62
	(040)	0.40	16.880	5.235	125	
	(130)	0.26	18.440	4.801	102	

stearate is normally a "classic" lubricant for PP, which can improve the mould release, melt flow and lubricity.[22] However, this study shows that stearate plays the same role of a nucleation agent as modified rosin, inducing the growth of α-crystal.

Effect of Additives on Electret Charge Behavior

TSD measurement is a prime technology to evaluate electret charge behavior.[23] Short-circuit TSD spectra for samples P0 and P2 are showed in Figure 4. As a comparison, Figure 4 also displays the TSD spectrum of un-charged sample P2 and no current peak is observed, implying that un-charged sample is not characteristic of an electret. As shown in Figure 4, electret samples start to release charge around 80°C, at which filtration efficiency of doped PP electret P2 just begins to decline but that of non-doped PP electret P0 has decayed rapidly as illustrated in Figure 2. It is also noticed from Figure 4 that TSD peak area for sample P2 are larger than that of sample P0, which indicates more trapped charge in stearate-doped sample. These results demonstrate that additive doping can enhance charge trap density and then enlarge the charge storage capacity. As it turns out in previous section that the doped sample P2 has larger crystallinity and more fine-grained crystallite than pure PP sample P0, which leads directly to higher charge trap density, so higher charge storage capacity gets realized.

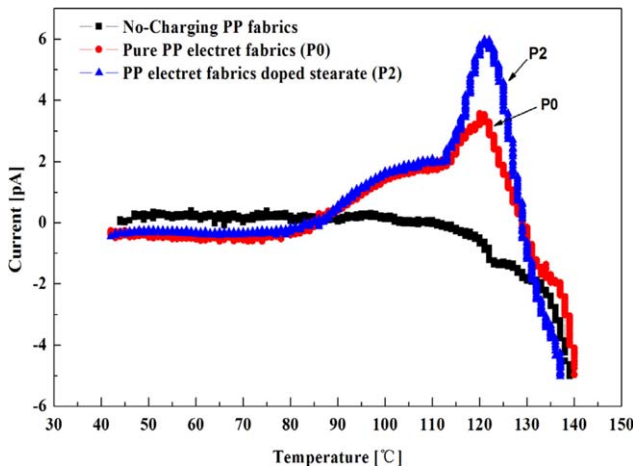

Figure 4. Short circuit TSD spectrum of melt-blown PP electret fabrics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 also illustrates that fast discharging begins at 112°C and the TSD current peak appears at 123°C for doped melt-blown PP electret fabrics. It is remarkable that the peak current of doped sample P2 is dramatically higher than that of non-doped sample P0. This may, to some extent, account for the high temperature stability of filtration efficiency in a certain range of temperature for doped PP electre, which still remains above 95% of its initial even at the temperature as high as 110°C, whereas pure PP electret only remains 58% of its initial at this temperature as shown in Figure 2. On the basis of the TSD results, it further proves that the outstanding filtration performance of doped samples mainly depends on its excellent electret charge behavior.

Analysis of Correlation Between Filtration Performance and Crystalline Structure

Correlation between filtration performance and crystalline feature is summarized in Table II. Better filtration performance can be ascribed to the modification of crystalline structure for doped melt-blown PP electret fabrics. When crystallinity increases and crystallite size decreases, both the initial filtration efficiency and its temperature stability gets improved. The crystallinity of pure PP fabrics is 14.7% and its initial filtration efficiency is 93.62%. After doping modified rosin or stearate, the crystallinity rises to 22.64% and 29.62%, and initial filtration efficiency increase to 99.43% and 99.68%, respectively. Furthermore, it is worth noticing in Table II that temperature stability of filtration efficiency also gets improved dramatically after doping additives.

As is well known, the outstanding filtration performance of melt-blown PP electret fabrics mainly originates from its excellent electret charge behavior. It has been pointed out in our

Table II. Correlation of Crystallinity and Filtration Efficiency η

Sample fabrics	Crystallinity (%)	Initial η (%)	η at 100°C (%)
P0	14.17	93.62	59.86
P1	22.64	99.43	96.67
P2	29.62	99.68	97.68

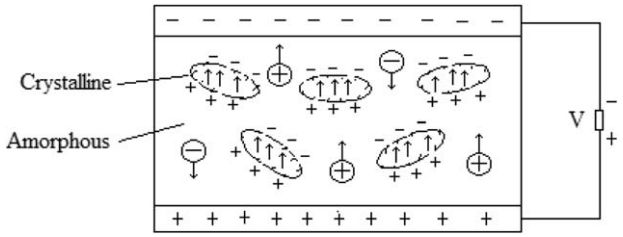

Figure 5. Schematic diagram of charge piled up at crystalline surface in semicrystalline polymer under DC field.

previous study that the drop of filtration efficiency and the decline of surface potential exactly display the same trend.[24] Therefore, the filtration efficiency mirrors the charge storage capacity for PP electret fabrics. The correlation between filtration performance and crystalline feature reflects the effect of crystalline structure on charge storage capacity. The increase of crystallinity and the refinement of crystallite for doped melt-blown PP electret fabrics can give rise to the increase of electret charge trap density. Therefore, charge storage capacity for electret gets raised (Figure 5).

As semi-crystalline polymer, PP fabrics are composed of crystallite and amorphous region introduced by twisting and branching. Many researchers have pointed out that charge traps, which mainly result from the interfaces between crystallites or between crystallite and amorphous region, play a major role in charge storage capacity.[25,26] The nature and density of the charge traps accordingly vary with processing condition and composition of melt-blown PP electret fabrics. On the basis of this idea, the charge profile of PP electret fabrics is adopted as in Figure 5. When PP fabrics are charged under DC field, the charge carriers tend to pile up on the surface of crystallite, where its normal drift is hindered due to the electrical conductivity difference between crystallite and amorphous region. As a result, the charge is immobilized and remains staying on the surface of crystallite. Generally there are two kinds of charge for electret, space charge and dipole charge. For PP electret, there only exists the space charge rather than the dipole charge. The space charge forms dipoles as a basic unit of every crystallite. These space-charge dipoles make the main source of charge trap for melt-blown PP electret fabrics. Charge trap density increases with the increase of crystallinity and the refinement of crystallite.

CONCLUSIONS

Two additives were doped to melt-blown PP electret fabrics at the concentration of 0.5 wt %. By XRD characterization, the crystalline structure of doped PP possesses the feature of larger crystallinity and more fine-grained crystallite as compared with that of non-doped PP. After doping, the crystallinity is 22.64% and 29.62%, respectively contrasting 14.17% for non-doped. At the same time, the crystallite size is smaller with 89Å and 86Å, respectively, for doped PP as a comparison with 107Å before doping in the direction vertical to lattice plane (110). This structure modification accounts for the improvement of electret charge storage behavior, which can be demonstrated by short-circuit TSD spectra. As a result, the filtration performance for doped melt-blown PP electret fabrics gets improved greatly. Although at room temperature, filtration efficiency only increased by 6%, the filtration efficiency of doped PP still remains above 95% of its initial with contrast to 58% for non-doped PP at elevated temperature as high as 110°C. This indicates that additive doping dramatically promotes the temperature stability of filtration efficiency in particular. We can draw the conclusion that outstanding filtration performance mainly depends on the excellent electret charge behavior. The filtration performance can be explained with TSD which relevantly reflects the charge storage behavior of melt-blown PP electret fabrics.

In conclusion, there exists interface between crystallite and amorphous region in melt-blown PP fabrics. The outstanding filtration performance mainly depends on its superior electret charge behavior. Doping additives such as stearate and modified rosin can give rise to the increase of crystallinity and the refinement of crystallite, thereby better filtration performance is achieved. After doping additives, the modification of crystalline structure leads to the improvement of electret charge storage behavior. The charge traps, which mainly originate from the interfaces between crystallite and amorphous region of melt-blown PP electret fabrics, play a major role in charge storage. The space charge forms a dipole as rigid as crystallite. This space-charge dipole makes the main source of charge trap, whose density increases with larger crystallinity and more fine-grained crystallite.

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