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Thermal and topographical characterization of polyester- and styrene/acrylate-based composite powders by scanning probe microscopy

Kaj Backfolk [a,*], Petri Sirviö [a,b], Petri Ihalainen [b], Jouko Peltonen [c]

[a] *Stora Enso Oyj, Imatra Research Centre, FI-55 800 Imatra, Finland*
[b] *Department of Physical Chemistry, Åbo Akademi University, Porthaninkatu 3-5, FI-20500 Turku, Finland*
[c] *Laboratory of Paper Coating and Converting, Åbo Akademi University, Porthaninkatu 3-5, FI-20500 Turku, Finland*

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Abstract

The thermal properties of two conventional polyester-based toners and a chemically prepared styrene/acrylate toner with different thermal histories were studied by scanning probe microscopy (SPM) and differential scanning calorimetry (DSC). The thermal transition temperatures detected by SPM agreed with the results of the DSC measurements. The validity of SPM for detecting thermal transitions was further confirmed by studying two amorphous reference polymers with different glass transition points (T_g) and three crystalline reference polymers with different melting points (T_m). When the toner sample was heated by the SPM probe above the glass transition temperature of the toner powder ($T_{probe} > T_g$), changes occurred in the surface topography and roughness causing different levels of local sintering of the particles. A set of roughness parameters calculated from the SPM image data were used to quantify the most essential features of toner surfaces. Environmental scanning electron microscopy (ESEM) was used to study the penetration depth of heat dissipated by the SPM probe. The probe-annealing was compared with oven-annealing in order to establish the effect of thermal history on the thermal properties of the materials.

Keywords: Thermal analysis; Toner; Binder; Glass transition temperature; Topography; DSC; ESEM; SPM

1. Introduction

Toner melting, sintering, spreading or leveling and penetration are the main physical stages associated with the fusing process in dry toner electrophotography [1,2]. The progress of these stages has been illustrated with oven-fused samples showing that melting and sintering of the toner particles occurs before fixing to the substrate [3]. The initial phases of the fusing process, i.e. melting and sintering are mainly dictated by the toner properties and fusing conditions. The subsequent spreading, leveling and penetration stage is a complex interplay between fusing conditions, toner properties and the physical and physico-chemical properties of the substrate. The spreading and leveling of toners on different substrates and the effect on print quality have been shown to be dependent not only on the fusing conditions but also on the surface energy of the substrate [4–7]. The substrate or surface compressibility may also affect the contact area, dwell time and fusing nip temperature [8]. Different opinions have been presented concerning the effect of surface roughness on the fusing fix [9,10]. The toner penetration depth is in the range of micrometers in roll fusing systems on uncoated paper [6,11], and this is obviously strongly influenced by the thermo-rheological properties of the toners.

The relationship between the rheological properties of toners and the fusing fix [12,13] suggests that toner leveling and maximum substrate contact are essential for toner adhesion. Since the surface roughness affects both toner packing and heat absorption ability, surface (toner/air) and interface (toner/substrate) temperatures should be optimal in order to achieve proper conditions for particle sintering and coalescence [14]. In addition, changes in fusing nip temperature in the printing direction due to local differences in thermal diffusivity [15], and cross-section temperature gradients caused by particle size effects [16] make it difficult to achieve optimal fusing conditions.

* Corresponding author. Tel.: +358 2046 23467.
E-mail address: Kaj.Backfolk@storaenso.com (K. Backfolk).

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Nevertheless, only a limited number of methods have been developed to gain information about toner properties at elevated temperatures related to their sintering, leveling and spreading behavior. Rheological characterization is often used to describe toner properties important for runnability and print quality. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been used for the thermal analysis of toners. The spreading of individual toner particles on different glass substrates has been studied in a microscope [4] and Lever and Price [17] have utilized micro-thermomechanical analysis (μTMA) and micro-modulated differential thermal analysis (μMDTA) to study the thermal properties of toner particles. In addition, thermal properties and glass transition temperatures of polymer and composite films have been studied by utilizing various modes of SPM, such as scanning thermal microscopy (SThM) [18–24], local thermal analysis (LTA) [25,26], friction (later) force microscopy [27–29], shear-modulated scanning force microscopy (SM-SFM) [30,31], scanning local acceleration microscopy (SLAM) [32], and various spectroscopic modes including force–distance measurements [33] and an SPM probe resonance frequency method by utilizing an SPM probe as a sensor for detecting thermal transitions [34–37].

A novel method for the thermal characterization of latex films utilizing scanning probe microscopy (SPM) was recently presented [38–40]. In this non-contact approach, the SPM probe is heated and the probe is utilized simultaneously as an actuator and a sensor. The heated probe both dissipates heat and detects the heat reflected from the sample. The resonance frequency (ω) of the probe oscillating above the sample surface is determined for different probe temperatures (T_p). The $\Delta\omega$–T_p curves can be used to detect thermal transitions in latex films as changes in the heat capacity of the samples [38]. The direction of the temperature gradient can be chosen, i.e. towards the sample (probe heating) or from the sample (sample heating), so that migration or evaporation from the bulk can be identified and taken into account.

In the present study, the SPM probe frequency method [38] has been used to determine thermal properties of dry toner powder samples. Two conventional toners consisting of a polyester binder and a chemically prepared toner containing styrene-butyl acrylate binder were studied. The SPM probe frequency method was validated by comparing thermal transition temperatures obtained by SPM with those obtained by DSC. In addition to the three toner samples, three crystalline polymers and two amorphous polymers were used as references. The various toner powder samples were also oven-annealed before SPM thermal analysis in order to establish the effect of sintering, i.e. thermal history, on the thermal properties of the materials. In addition to thermal analysis, FTIR spectroscopy, and topography and phase contrast imaging of toner tablet surfaces were studied. A set of roughness parameters calculated from the SPM image data were used to quantify the most essential features of toner surfaces. Environmental scanning electron microscopy (ESEM) was used to study the penetration depth of heat dissipated by the SPM probe.

2. Experimental

2.1. Materials

Three types of commercial toners were collected directly as powders from the cartridges of different electrophotographic machines. Toner 1 was a conventional black toner with a polyester type binder, toner 2 was a conventional cyan toner with a polyester type of binder similar to that of sample 1, and toner 3 was a chemically prepared toner containing a styrene/butyl acrylate binder. The toner powders were pressed to a tablet before determining the thermal properties with SPM. In order to study the effect of thermal history, the pressed toner tablets were heat-treated or sintered as a film on mica in an oven at 160 °C for 10 min (referred to as oven-annealing).

Three crystalline reference polymers used for the thermal study were; a copolymer of ethylene and methacrylic acid (15 wt%) (Nucrel® 925, Dupont™), a copolymer of ethylene and methacrylic acid (11 wt%) (Nucrel® 699, Dupont™), and a ethylene-vinyl acetate (28 wt%)/acid terpolymer resin (Elvax® 4260, DuPont™), denoted reference 1, 2, 3, respectively. Two amorphous styrene/butadiene latex polymers with low and high-glass transition temperatures were used. The first copolymer, denoted reference 4, consisted of a mixture of styrene (82.6 wt%) and butadiene (15.0 wt%) and the second copolymer, denoted reference 5, consisted of a mixture of styrene and butadiene with a ratio of 92.8:5.0 wt% [38]. Both were supplied by Omnova Solution Inc. (USA).

2.2. Methods

A Nanoscope IIIa (Digital Instruments Veeco Metrology Group, Santa Barbara, CA) SPM equipped with a MultiMode™ high temperature heater was used for imaging and thermal analysis of the sample surfaces. Both the sample and the cantilever (probe) can be heated, either simultaneously or separately, from ambient temperature up to 250 °C [41–43]. A specialized AS-130VT scanner including a resistive type heater and a thermocouple for sample temperature measurement was used. The scanner contains a water–fluid cooling system to protect the piezo elements from overheating. Uncoated 0.01–0.025 Ω cm antimony (n)-doped silicon probes (model LTESP, Veeco) were used for thermal analysis and imaging. The probes were installed in a special probe holder with options for cantilever oscillation and probe heating, gas purging and external sensor access. The microscope was placed on an active vibration isolation table (MOD-1M JRS Scientific Instruments, Switzerland) mounted on a massive stone table to eliminate external vibrational noise.

All the images (512 × 512 pixels) were captured using intermittent contact under ambient conditions (25 ± 3 °C, 35 ± 5% RH) without filtering. The free amplitude of the oscillating cantilever (off contact) was set to 70 ± 5 nm. The engage procedure caused a shift in the resonance frequency, which was taken into account. The new resonance frequency for the tip in contact was determined and used as the operating frequency. A damping ratio (measuring amplitude/free amplitude) of 0.5–0.6 was used for imaging. The scanning probe image processor