Electron Microscopy Observation of Paper and Nanomaterials Using the Hitachi SU5000 FE/VP-SEM and the Hitachi HT7800 120kV TEM coupled with HILEM 1000 Ionic Liquid for Sample Preparation

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The visualization of specimens in a hydrated / wet state is a key factor for many applications in electron microscopy to appropriately analyze compositional and morphological characteristics. To address this aspect and better determine shape, size and surface characteristics for different types of materials, analyses using state-of-the-art Hitachi SEM and TEM instrumentation coupled with Hitachi ionic liquid HILEM IL 1000 [1-4] for sample preparation are being developed. Fibers and material fillers in vintage as well as recent stocks of U.S. manufactured cotton-based paper [5], novel nanoparticles in aqueous solutions [6, 7], and NIST Standard Reference Materials (SRMs), polystyrenes in water, are being examined to develop advanced methods for imaging these types of materials. These are possible candidate matrices for new reference materials that will be dimensionally and morphologically characterized by various methods, including electron microscopy.

SEM of Paper. Papermaking involves the use of mineral fillers that are added to a cellulosic fiber matrix prior to being formed into sheets and contain water-insoluble particulate substances on the order of approximately 0.1 μm to 10 μm [8]. The particle shape of fillers can be used in forensic investigations of paper origin or authenticity. We have applied the Hitachi SU5000 field emission variable pressure SEM to explore the detailed structure of the paper matrix and its composition. The SU5000 offers unique capabilities to provide high resolution at low accelerating voltage as well as high performance with high probe current. To lessen localized brightness / charging that might result from the nonuniformity on the surface of paper samples, the IL1000 was also applied to uniformly wet the paper's native conformation while limiting localized sample charging. Figure 1 shows SU5000 backscatter electron (BSE) and ultra-variable-pressure secondary electron detector (UVD) images of 25% cotton paper with the IL1000. The SEM imaging with the SU5000 provides enhanced profiling of paper via exploration in both the BSE and UVD modes when coupled with IL1000. Fine threads protruding from the surface of the paper along with clear and smooth surface features can be easily observed. Additionally, paper samples are under investigation for mineral composition using the Hitachi Advanced Mineral Identification and Characterization System (AMICS), the latest software package for automated identification and quantification of minerals and synthetic phases using energy dispersive x-ray spectrometry.

TEM of Nanomaterials. Observations of aqueous material-based particles in the stable, non-toxic IL1000 ionic fluid demonstrate this approach to sample preparation is an excellent choice for TEM imaging of samples that contain water or have requirements for a liquid environment. The Hitachi HT7800 120 KV TEM is being used to examine SRMs 1963a and 1964, 100 nm and 60 nm polystyrene spheres in water, respectively, suspended in IL1000. A final v:v concentration of 20% HILEM

IL1000:nanoparticle solution was placed directly onto a copper grid with holey carbon only. Excess fluid was removed via filter paper, leaving the remaining ionic liquid to form menisci containing nanoparticles in the voids of the holey carbon [1]. Figure 2 shows each material in detail with clear, smooth images of the spheres.

References:
[1] JP Kilcrease and E Voelkl, Proceedings of Microscopy & Microanalysis (2016) p. 810.
[2] JP Kilcrease, O Takagi and G Bauchan, Proceedings of Microscopy & Microanalysis (2016) p. 246.
[3] A Muto *et al*, Proceedings of Microscopy & Microanalysis (2016) p. 232.
[4] M Sakaue *et al*, Proceedings of Microscopy & Microanalysis (2014) p. 101.
[5] M Kombolias *et al*, Proceedings of TAPPI's PaperCon (2018) in press.
[6] J Ettedgui, JJ Kasianowicz and A Balijepalli, JACS **138** (2016) p. 7228.
[7] J An et al., Polymer (2011) p. 5746.
[8] MA Hubbe and RA Gill, Bioresources **11** (2016) p. 2886.
[9] Certain commercial equipment or materials are identified to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

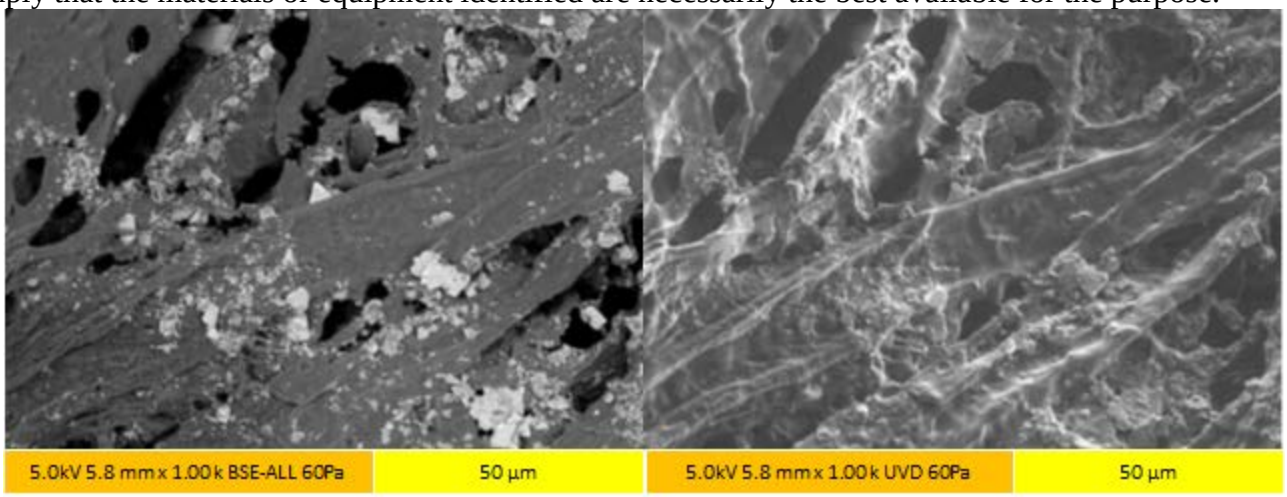

Figure 1. Hitachi SU5000 FE/UVD SEM images in BSE (left) and UVD (right) modes with the use of the ionic liquid HILEM IL 1000 on samples of 25% cotton paper, scale at 50.0 µm.

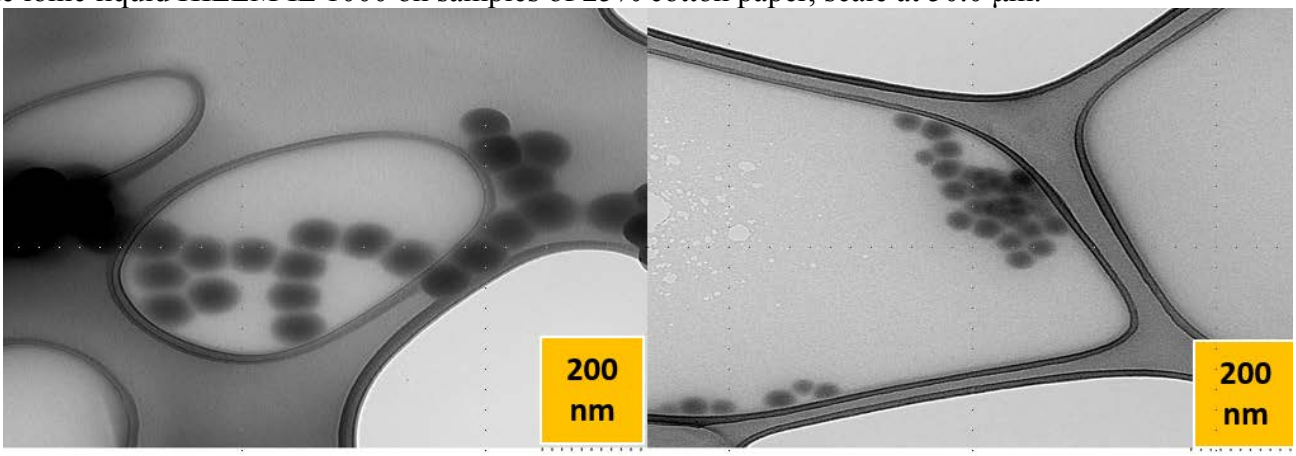

Figure 2. Hitachi HT7800 120 KV TEM images with the use the ionic liquid HILEM IL 1000 on SRM 1963a (left, 100 nm polystyrene spheres) and 1964 (right, 60 nm polystyrene spheres), scale at 200 nm.