Structure and electrical properties of polymer core-shell latex systems revealed by helium ion microscopy

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The emerging fields of molecular and printed electronics, organic and hybrid photovoltaics create demand for development of solution processed intrinsically conducting polymers (ICP) [1,2]. Polyaniline (PANI) and polythiophenes (PT) are two examples of ICP's that demonstrate attractive characteristics, especially when prepared as nanostructured systems (nano-wires, nanoparticles). These polymers can also be blended with common, stable polymers to make composites with a combination of useful properties (so-called multifunctional materials) [3,4]. In this work we discuss peculiarities of the structure and electrical properties of two core-shell systems subjected to various fabrication protocols. The features of the electrical behavior are revealed by a combination of helium ion microscopy (HIM) and current-voltage characterization. The systems under study have a polar ferroelectric polyvinylidene fluoride (PVDF) as a core and electrically conducting or semiconducting shells (PANI or PT).

Application of HIM allowed identification of the polymer components, visualization of electrically conductive percolation network of PANI or PT and its variation due to thermal annealing and/or interaction with the environment. We discuss peculiarities of specific contrast formation in HIM imaging due to differences in local electrical conductivity of the components. Application of ion etching available in HIM in combination with nanoscale imaging is demonstrated. This approach provides additional advantages and a unique possibility for characterization of complex systems with buried polymer-polymer interface (junction). Proper control of the junction in core-shell systems is a critical factor in optimization of the system's performance.

We demonstrate that the polymer core-shell systems under study offer an interesting universal platform for development of nanostructured multifunctional materials. They can be used for preparation of conducting and semiconducting polymer films having promising non-linear electrical and photovoltaic properties. The same approach can be also used for development of active components for chemical sensors with enhanced sensitivity to some analytes (like ammonia). HIM is proved to be a powerful tool for characterization of not only the morphology but also charge distribution and conductivity properties on the nanoscale.

REFERENCES

- 1. Pron, A.; Rannou P. Prog. Polym. Sci. 2002, 27, 135.
- 2. Grimsdale A.C.; Chan K.L.; Martin R.E.; Jokisz P.G.; Holmes A.B. Chem. Rev. 2009, 109, 897.
- 3. Armes, S.P. Colloidal Dispersions of Conducting Polymers (1998) Handbook of Conducting Polymers, 2nd Ed. Ed: T. A Skotheim, R. L. Elsenbaumer, J. R. Reynolds, Marcel Dekker, New York, Ch. 17.
- 4. Pud A.; Ogurtsov N.; Korzhenko A.; Shapoval G. Prog Polym Sci 2003, 28, 1701.



Fig. 1. (a) TEM image of PVDF-PANI core-shell particles. PANI coating (~20 nm thick) bridges neighboring particles of PVDF (~200 nm in diameter). (b-d) HIM images representing various fabrication protocols. (b) annealed sample showing formation of a porous composite material with an electrically-conductive percolation network of PANI due to sintering of polymer particles at elevated temperature. (c) As-prepared PVDF-PANI sample. (d) Annealed sample, exposed to ammonia vapors. The electrical conductivity of PANI shell is reduced ~30 times as a result of its exposure to ammonia as revealed by HIM and I-V measurements. Variation of the surface conductivity due to degradation of the percolation network in the ammonia exposed sample can be clearly seen in HIM.