



Transport Analysis in Polymeric Liquids and Films: Investigations in Ionic Mobility Isolation Techniques and Permeability Control

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Abstract

An *in situ* measurement technique that isolates the mobility of charge carriers is described and analyzed. The technique allows significant improvement over conductivity measurements to monitor changes in the physical properties and state of a material as it cures. This is essential in systems where N_i , the number of charge carriers, cannot be assumed constant such as during cure of epoxies, urethanes and polyimides.

Currently, there is an assumption made in the literature that the number of charge carriers present in a curing material is constant when conductivity is used as an *in situ* measurement technique to monitor changes in mobility (and thereby viscosity). This assumption is widely used, for example when dielectric conductivity measurements are correlated with changes in properties such as viscosity. Ion mobility, time of flight (ITOF) measurements, which are described here, are an appropriate technique to isolate and measure particle mobility due to changes in the state of the material. Furthermore, the ITOF technique, coupled with the measurement of σ , the ionic conductivity, allows one to measure *separately* changes in the mobility and the number of charge carriers due to curing or changes in temperature. This is possible since conductivity is the product of the number of charge carriers and their mobility. Length of pulse, strength of applied field, sensor geometry, and temperature/viscosity are examined to determine optimum parameters of measurement for both a simple non-curing system, and more complex, hydrogen-bonded epoxy.

The second focus of this thesis is our recently developed single stage *in situ* synthesis of hybrid membranes comprised of nanometer- sized metal and metal oxide particles in polyimides. The major goal is development of polymer based structural materials designed to achieve exceptional performance properties regarding gas permeability and gas separation selectivity, particularly in regard to their thickness, modulus, and strength to weight ratio. We investigate hybrid inorganic-polyimide films where the nanoparticle inorganic phases are of two types: 1) nanometer-sized rare earth (lanthanum, gadolinium and holmium) oxide molecular clusters and 2) nanometer-sized palladium and silver metal clusters. For the polymeric phase we used aromatic poly(amic acid)s-polyimides because of their strength and chemical and thermal stability. Nanoparticle-polyimide hybrid films were synthesized by extension of novel methods. They are distinctive in that they are *in situ* and single step routes to the uniform distribution of nanoparticles in the polyimide. This method is important because it disperses the nanoparticles uniformly within the film, and under certain conditions it allows for preparation of surface metalized films with metals such as palladium and silver. Our *in situ* procedure gives metal-polymer adhesion significantly stronger than can be accomplished by the physical vapor deposition. Appropriate selection of the cure time-temperature and cure gas environment may control the size and dispersion of nanoparticles in the film and the presence, size and thickness of nanoclusters at the surface and in the bulk.

