

Molecular Migration in Polyvinyl Acetate Matrix: Impact of Compatibility, Number of Migrants and Stress on Surface and Internal Microstructure

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Abstract : Migration of small molecules to, and across the surface of polymer matrices is a little-studied problem with important industrial applications. Tackifiers in adhesives, flavors in foods and binding agents in paints all present situations where the function of a product depends on the ability of small molecules to migrate through a polymer matrix to achieve the desired properties such as softness, dispersion of fillers, and to deliver an effect that is felt (or tasted) on a surface. It's been shown that the chemical and molecular structure, surface free energies, phase behavior, close environment and compatibility of the system, influence the migrants' motion. When differences in behavior, such as occurrence of segregation to the surface or not, are observed it is then of crucial importance to identify and get a better understanding of the driving forces involved in the process of molecular migration. In this aim, experience is meant to be allied with theory in order to deliver a validated theoretical and computational toolkit to describe and predict these phenomena. The systems that have been chosen for this study aim to address the effect of polarity mismatch between the migrants and the polymer matrix and that of a second migrant over the first one. As a non-polar resin polymer, polyvinyl acetate is used as the material to which more or less polar migrants (sorbitol, carvone, octanoic acid (OA), triacetin) are to be added. Through contact angle measurement a surface excess is seen for sorbitol (polar) mixed with PVAc as the surface energy is lowered compare to the one of pure PVAc. This effect is increased upon the addition of carvon or triacetin (non-polars). Surface micro-structures are also evidenced by atomic force microscopy (AFM). Ion beam analysis (Nuclear Reaction Analysis), supplemented by neutron reflectometry can accurately characterize the self-organization of surfactants, oligomers, aromatic molecules in polymer films in order to relate the macroscopic behavior to the length scales that are amenable to simulation. The nuclear reaction analysis (NRA) data for deuterated OA 20% shows the evidence of a surface excess which is enhanced after annealing. The addition of 10% triacetin, as a second migrant, results in the formation of an underlying layer enriched in triacetin below the surface excess of OA. The results show that molecules in polarity mismatch with the matrix tend to segregate to the surface, and this is favored by the addition of a second migrant of the same polarity than the matrix. As studies have been restricted to materials that are model supported films under static conditions in a first step, it is also wished to address the more challenging conditions of materials under controlled stress or strain. To achieve this, a simple rig and PDMS cell have been designed to stretch the material to a defined strain and to probe these mechanical effects by ion beam analysis and atomic force microscopy. This will make a significant step towards exploring the influence of extensional strain on surface segregation, flavor release in cross-linked rubbers.

Keywords : polymers, surface segregation, thin films, molecular migration

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