NEW ANALYTICAL DEVELOPMENTS FOR ELASTOMERS WEATHERING

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Abstract

Elastomers are widely used in automotive, aeronautic and electronic industries. The long term behaviour in different environments is studied because initial properties must be retained for several years under thermal or photochemical exposure. The weathering induced oxidation or/and cross-linking reactions, followed by different analytical tools.

The work presented here concerns two elastomers:

- a dienic elastomer (EPDM : Ethylene Propylene Diene Monomer)
- a siloxane (PDMS : polydimethyl siloxane)

Their chemical and physical evolutions are analysed by several techniques: FTIR spectroscopy by reflection, thermal analysis (DSC) coupled with thermoporosimetry, photo-DSC, thermogravimetric analysis (ATG) coupled with IRTF, hardness measurements and water permeability, densimetry and viscosity measurements.

We have specifically developed coupled techniques for a better understanding of polymer ageings. The complementary nature of these techniques helps to analyse various path ways of degradation (oxidation, cross-linking and chain scission), depending on the nature of the elastomer. The ability towards oxidation in the case of usual dienic elastomer was always identified by IR spectroscopy but cross-linking reactions are more difficult to understand. DSC coupled with thermoporosimetry permits us to differentiate the evolution of elastomer network. Post-cross-linking takes

place systematically for EPDM and silicone rubber. The DSC-thermoporosimetry measurements of the mesh size distribution gave a comparison of cross-linking densities for each elastomer [1]. It is a calorimetric technique used for the visualization of the material texture by studying the phase transitions (crystallization, melting or other change of state) undergone by the swelling solvent (cyclohexane) trapped in the polymeric network. The transition temperature of this confined solvent depends on the characterisation of the surrounding polymeric swollen network. The thermoporosimetry has essentially been applied to rigid porous substrates [2]. It is assumed that a polymeric gel is equivalent to a three dimensional network of adjacent cells that is called mesh. The solvent swells the crosslinked polymer until an equilibrium state is reached. It forms a swollen gel where the solvent is present under two environments : the confined solvent which is trapped inside the gel and the part of solvent which remains out and represents the excess (free solvent). The free solvent behaves like a pure solvent in term of phase transitions. On the other hand the confined solvent undergoes the phase transitions at different temperatures depending on the characteristics of surrounding polymeric network and especially depending on the size of the network mesh. The difference in the transition temperature T (given by DSC) between free and confined solvent can be related to the size of the mesh for elastomers. The choice of the swelling solvent will be discussed.

Another coupled technique ATG-FTIR was used to determine the thermal stability of filled compositions and to identify the volatile products formed during degradation [4]. The gaseous products coming from TGA are transferred though a heating tube in a gas cell and characterized by FTIR.

The initial silicone material (unaged sample) shows a distribution of mesh sizes with two peaks. Different cuts (180 m thick slices) from the surface of the rubber sheet have been characterized. We can clearly show that most meshes have a radius (distance between cross-links) around 200Å, the other mesh size is around 700Å. After photochemical or thermal ageings we obtain different distributions. We can present the evolution of EPDM and PDMS upon ageing. Post cross-linking and chain scission reactions are finally revealed by hardness mesurements and DSC-thermoporosimetry after usual ageings (photochemical, thermal). An essential consequence of post-cross-linking is the modification of mechanical properties. The differences between ageing mechanisms are quite significant and are discussed in the communication. We then try to compare the behaviour and the properties of the two elastomers. We can show the

complementary approach of each analytical tool. We finally try to estimate the accuracy of DSC-thermoporosimetry technique.

References

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