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## Summary

Polymeric networks have a broad application range as medical materials, rubbers, structural plastics, coating, *etc.* As the application of these polymeric networks depends of the properties which are directly related to their chemistry, it is important to have techniques to characterise the structural network parameters, such as the mean molecular weight of the chains between cross-links (network density), the molecular weight distribution of the polymeric backbone chains and the (im)perfections of the network.

The objective of the study described was to investigate the analysis of the chemical network structure of peroxide cross-linked rubber networks and chemically cross-linked di-acrylate systems, using an indirect approach. Different indirect approaches are used to obtain insight in the chemical network structures of these cross-linked systems: hydrolysis, pyrolysis and the use of model compounds.

Hydrolysis, followed by analysis with aqueous size-exclusion chromatography (SEC) on-line coupled to reversed-phase liquid-chromatography (LC), turns out to be a very powerful tool to determine the concentration and the molecular weight distribution of the chains between cross-links and the acrylic backbone chains in the different di-acrylate/mono-acrylate networks. Insight in the total network structure was obtained by analysis of the starting materials, combined with the analysis of the extractables of these acrylate networks. The acrylate network structure could be expressed in network parameters such as the degree of cross-linking and the network density. The latter was compared with results obtained from solid-state nuclear-magnetic resonance (NMR) and dynamic mechanical analysis, which reveal similar network densities for the different di-acrylate/mono-acrylate networks studied.

In the case of di-methacrylate/styrene networks, the concentration and molecular weight distribution of the styrene/methacrylic copolymeric backbone chains, isolated in a straightforward way after hydrolysis of the network at extreme conditions, followed by SEC analysis, give insight in the network structure. Liquid-NMR analysis of these hydrolysis products reveals the mean styrene and mean methacrylate sequence length of the backbone chains. Not only does the use of these techniques give insight in the final network structure itself, but also in the influence of the concentration styrene and a radical-transfer agent on it.

The different stages of hydrolytic degradation of chemically cross-linked poly-

(*D,L*-lactide-*co*-glycolide 50/50)-diacrylate film, were characterised using SEC and liquid chromatography–mass spectrometry (LC-MS). Detailed information was obtained regarding the concentrations and oligomeric compositions of different solubilised oligomeric and polymeric products during the different stages of degradation: extraction, network attack, network penetration, bulk degradation, and finally release of persistent network fragments.

These studies mentioned above show that hydrolysis followed by chromatographic and mass spectrometric techniques, turns out to be a powerful tool to enhance the understanding of chemical network structure of acrylate networks.

In the case of a peroxide-cured terpolymer of ethylene, propylene and diene monomer (EPDM), which cannot be hydrolysed, the network structure was studied using low-molecular-weight model compounds, which mimicked the peroxide cross-linking reactions of EPDM. Both gas chromatography–mass spectrometry (GC-MS) and comprehensive two-dimensional GC–MS (GC×GC–MS) analyses have been employed to analyse the different isomeric reaction products. The MS-fragmentation patterns and the GC-elution patterns are investigated in high detail to identify the different isomeric reaction products. This study with model compounds has led to a more accurate description of the peroxide cross-linking scheme of EPDM and valuable insight in the cross-linking mechanism (H-abstraction reactivities, steric hindrance, *etc.*). In conclusion, the approach to use low-molecular-weight model compounds has proven to be an excellent means to study the cross-linking mechanism of EPDM.

Pyrolysis followed by analysis is another indirect approach to study networks. The feasibility of thermal degradation methods for the characterisation of network structures was studied using chemically cross-linked acrylates. Techniques such as thermogravimetric analysis and differential scanning calorimetry give insight in the decomposition temperature, while pyrolysis (Pyr) followed by direct mass spectrometry analysis (Pyr-MS) shows different series reflecting the chains between network junctions and the backbone chains. Similar results are obtained using matrix-assisted laser desorption ionisation followed by time-of-flight mass spectrometry, in combination with a ‘solid’ sample preparation. To improve the reliability of identification of the various degradation products, LC-MS analysis upon pyrolysis was performed. Both off-line Pyr-LC-MS and on-line-Pyr-LC-MS analyses show thermal degradation products of cross-linked acrylates that support the proposed acrylate network

structure and give insight in the chemical composition. Thermal degradation temperatures, as observed by Pyr-MS, show a linear relation with the network density of both di-acrylate/mono-acrylate and di-methacrylate/styrene networks.

Summarising, it can be concluded that indirect approaches, using model compounds or hydrolysis followed by chromatographic analysis, are very powerful tools to study network structures and network parameters. Hydrolysis, as a sample preparation technique, followed by chromatography can be used to study chemical degradable networks such as acrylate networks, while model compounds are more suitable as sample preparation for networks such as EPDM which do not have hydrolysable groups.