

Abstract

This doctoral dissertation addresses the industrially viable and environmentally sustainable preparation of thermoreversibly crosslinked polymers and nanocomposites. First, the state of the art on Covalent Adaptable Networks (CANs) and composites is presented, in order to give to the reader a clear background into which this work lies. The two main classes of CANs, associative and dissociative, according to the network rearrangement process, are presented and discussed with a variety of examples, in the case of both polymers and composites. After showing the differences between the two approaches, the choice of a dissociative system is justified and the experimental work is presented. Three different groups of dissociative CANs based on the thermoreversible crosslinking via Diels-Alder (DA) reaction of three different polymers (a Styrene Maleic Anhydride (SMA) copolymer, a Polyethylene grafted with Maleic Anhydride (PEgMA) and an Ethylene-Propylene Rubber grafted with Maleic Anhydride (EPRgMA)) were prepared via melt blending as an environmental-friendly alternative to traditional synthesis in organic solvents. Functionalization of the polymers with furan groups was previously validated in solvent for SMA, then performed in a melt blender for the three polymers. The achievement of the functionalization was assessed by FT-IR spectroscopy. The obtained grafted polymers (SMAgF, PEgF and EPRgF) were subsequently mixed with different amounts of bismaleimide (BM or BM1) in a micro-extruder. Crosslinking was assessed by FT-IR spectroscopy and confirmed for EPRgF-BM CANs, which were further characterized for physical properties. Crosslinking degree was assessed by solubility at room temperature, while the thermoreversible character of the network was confirmed by a solubility test at 110 °C and by re-molding via hot-pressing. Mechanical and thermomechanical properties of the obtained rubbers showed potential to compete with conventionally crosslinked elastomers, with stiffness in the range 1-1.7 MPa and strain at break in the range 200-500%, while allowing recycling via a simple melt processing step.

Reduced Graphene Oxide (rGO) and Silica (Si) nanoparticles were selected as suitable nanofillers for EPR, due to the central role of carbon and silica fillers in rubber industry and the reinforcement provided by nanoparticles at low loadings.

Possible DA reaction on carbon nanoparticles, described in the state of the art, was explored via a model reaction between Graphite NanoPlates (GNP) and MA, both following a solvent method already used in literature (GNP-MA_sol) and using a new developed vapor method which does not involve the use of solvents (GNP-MA_vap). Then the prepared GNP-MA adducts were characterized via TGA, DSC, XPS, FT-IR and Raman spectroscopy, evidencing the presence of interacting MA on GNP in GNP-MA_vap with indications of covalent DA grafting. Nanocomposites based on the thermoreversible rubber were prepared with rGO, showing significantly increasing stiffness up to ca. 8 MPa, ~2-fold increased strength, and thermal conductivity up to ~0.5 W/(m·K). To overcome the problem of high viscosity in the melt during processing, an alternative processing technique called Press&Fold (P&F) method was used with the aim of rising the content of rGO in the nanocomposite, unfortunately with unsatisfying results due to matrix degradation. Regarding Sil nanocomposites, a maleimide-functionalized silica (Sil-M) was prepared and then mixed with EPRgF. Mechanical properties of EPRgF/Sil-M were compared to unfunctionalized EPRgF/Sil to demonstrate the role of DA crosslinking on mechanical properties. Furthermore, the combination between Sil-M and BM as a conventional DA crosslinker was investigated, to optimize crosslinking degree and materials performances.

Overall, results reported in this work demonstrate the possibility to develop a new class of recyclable nanocomposite rubbers for the substitution of conventional rubbers, which are currently causing major problems in the management of rubber products at their end-of life, using an industrially viable e sustainable process.