Sulfur-Dipentene polysulfides: from industrial waste to sustainable, lowcost materials

Selena Silvano, a Incoronata Tritto, a Simona Losio, a Laura Boggioni b

^a CNR-SCITEC Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", via A. Corti, 12, 20133 Milano, Italy

selena.silvano@scitec.cnr.it

Reduction of fossil fuel consumption and shift towards renewable feedstock are among the goals of a sustainable development. In particular, the reuse of industrial wastes as starting materials could strongly minimize the impact of productive activity on environment. [1]

Large volumes of elemental sulfur derived from oil industry are stored unused, causing the global "excess sulfur problem". [2] In the last few years an interest in exploring the use of sulfur as a low cost starting material for the synthesis of sulfur rich-polymers with interesting optical, electrical and antibacterial properties has emerged. [3,4]. Dipentene is a low cost, bio-based mixture, produced from citrus oil in large scale.

Here, we report the valorization of these industrial wastes: for the first time, the synthesis of poly(S-dipentene) with a sulfur content greater than 50 wt % by catalytic inverse vulcanization in the presence of zinc-based accelerators was investigated. Accelerators, probably acting as phase transfer, reduced the time required for mixing of dipentene and melted sulfur; the best results were obtained with zinc tetrabutyl-bis(phosphorodithioate). [5]

In order to improve the poly(S-dipentene) stability, a second bio-based crosslinker was added. Three bio-based dienes, garlic oil (GO), diallyl disulfide (DAS) and myrcene (MYR), were used as crosslinker in post-polymerization of poly(S-dipentene). Stable *ter*-polymers with depressed depolymerization reactions were achieved by adding 10 wt % of MYR, GO or DAS. *Ter*-polysulfides produced are soft solids with T_g values between -1 and 4 °C. In order to make processable *ter*-polysulfides and to give them shape persistence for possible applications, preparation of polystyrene-polysulfide blends was investigated. Polystyrene blends were prepared via the salt templating technique by mixing poly(S-dipentene-DAS) and polystyrene (50/50 wt %) solubilized in chloroform. Porous, homogeneous and processable polystyrene-poly(S-dipentene-DAS) blends were obtained with T_g value of 44 °C. These blends have shape persistence, a fundamental requirement to prepare an object. They were found to be able to remove ferric ions from aqueous solution for application in wastewater purification. Thus, green-polysulfides were achieved, which represent an economical alternative to polysulfides synthesized from enantiomeric limonene. [3]

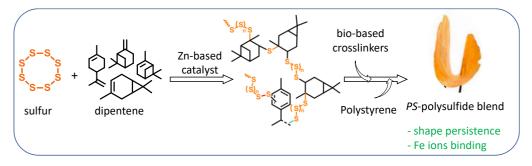


Figure 1. Polysulfides production from elemental sulfur and dipentene

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