



Cross-linking of rubber in the presence of multi-functional cross-linking aids via thermoreversible Diels-Alder chemistry

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ABSTRACT

Furan-functionalized polyketone (PK-FU) was added to a furan-functionalized ethylene-propylene rubber (EPM-FU). The mixture was subsequently cross-linked with a bismaleimide through Diels-Alder chemistry in order to improve the mechanical properties of the rubber. Infrared spectroscopy showed the reversible interaction between both polymers and the bismaleimide cross-linker. Likewise, mechanical measurements indicated the re-workability of the mixtures with no evident differences in storage modulus and mechanical properties after several heating cycles. The cross-link density and mechanical properties, such as hardness, tensile properties and compression set, could be modulated by changing the degree of furan functionalization of PK-FU and the PK-FU loading in the blends. It is concluded that PK-FU has some characteristics of an inert filler, but mainly acts as a multi-functional cross-linking aid, enabling larger amounts of bismaleimide to cross-link EPM-FU.

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1. Introduction

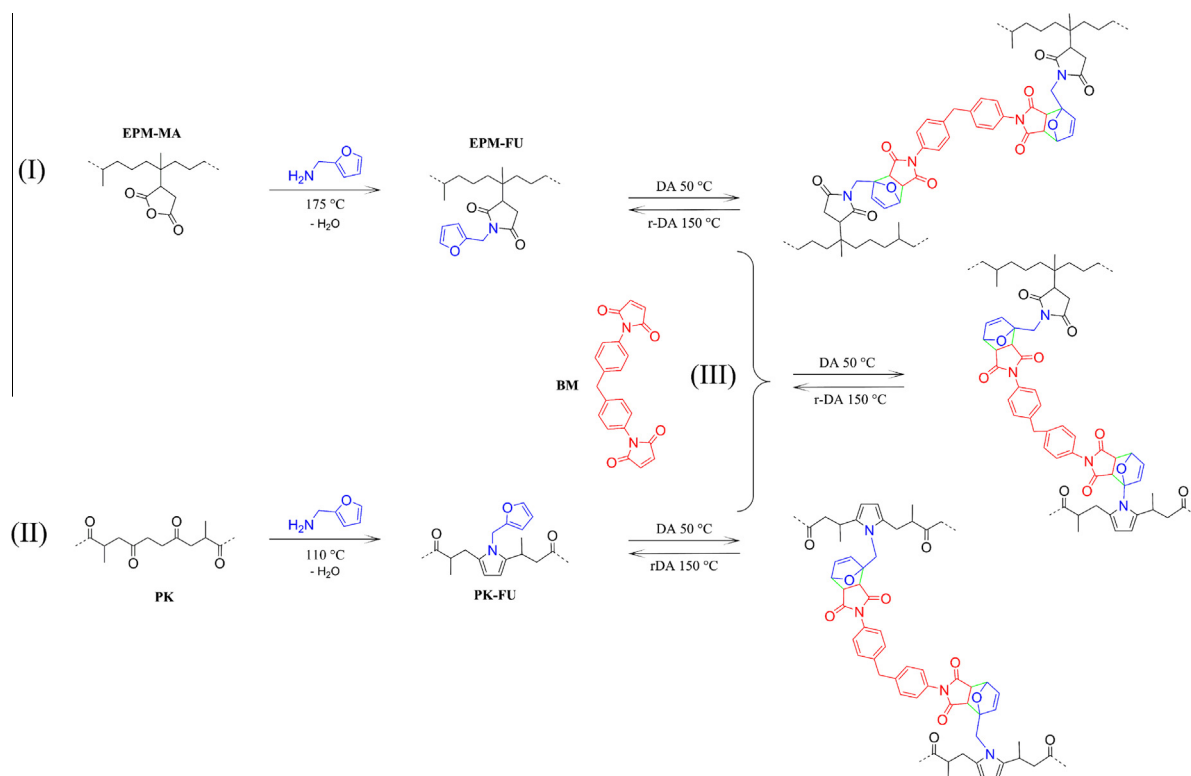
EPM copolymers are synthetic elastomers that are obtained from the copolymerization of ethylene and propylene. EPDM rubbers contain a third monomer, i.e. a non-conjugated diene (usually 5-ethylidene-2-norbornene or dicyclopentadiene), introducing a small amount of pendant unsaturation for sulphur vulcanization. The saturated polymer backbone provides EP(D)M rubbers with inherent resistance against degradation by heat, oxygen, ozone and light, especially where compared to diene rubbers such as natural rubber and polybutadiene rubber [1,2]. EP(D)M rubber is used in a large variety of outdoor and elevated-temperature applications, ranging from automotive to building and construction. Like other rubbers, EP(D)M rubber is compounded with (reinforcing) fillers and plasticizers, and subsequently shaped and cross-linked. Cross-linking is typically achieved via sulphur vulcanization or peroxide curing, resulting in an elastic, three-dimensional polymer network that cannot be melted or reprocessed [2,3]. Simple mechanical grinding of waste rubber produces low quality feedstock for virgin rubber [4]. Meanwhile, pyrolysis and incineration are downcycling methods that are still associated with environmental issues. The irreversibility of the conventional cross-linking processes constitutes the major restraint in the recycling of waste rubber. Devulcanization of sulphur-vulcanized rubber, i.e. the cleavage of carbon-sulphur or sulphur-sulphur cross-links, has been widely studied [5–7] and is commercially practiced, but may cause a considerable amount of bond scission in the polymer main chain [2,7], which is detrimental for the performance of the recyclate compared to the virgin material.

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In this context, the development of ionomers, thermoplastic elastomers (TPEs) and thermoplastic vulcanizates (TPVs) [8,9] has represented a major advancement, since these products combine the processability of thermoplastics at relatively high temperature with the elasticity of cross-linked rubbers at service temperature. The polymer backbone of TPEs, for example (hydrogenated) styrene/butadiene/styrene [S(E)BS] triblock copolymers, consists of “hard” and “soft” segments, which phase separate at low temperature, resulting in two phases with a high and a low glass transition temperature (T_g), respectively [8,10]. Cross-linking in TPEs does not occur through chemical bonds, but because the hard domains “cross-link” the soft matrix. The hard domains soften at high temperature, i.e. the “cross-links are broken”, and the TPE becomes melt processable [2]. The disadvantage of TPEs resides in their poor high-temperature performance, since this is factually limited by the T_g of the hard segments (e.g. around 80 °C for S(E)BS [11]).

An alternative approach for the recycling of thermoset cross-linked polymers is thermoreversible cross-linking. In particular, the Diels-Alder (DA) reaction has gained major interest for this purpose, because of the relatively fast kinetics and the mild conditions for (de)cross-linking without the need of a catalyst [12–15]. DA cross-linking proceeds via the cycloaddition of a diene to a dienophile, typically a furan and a maleimide, at relatively low temperature (e.g. 50 °C) [16–19]. De-cross-linking via the retro DA reaction is favored at high temperature (typically above 100 °C), thus allowing the material to be reshaped or recycled. In a previous study a commercial, maleated EPM (EPM-MA) was grafted with furfurylamine (FFA), yielding EPM-FU, which was then cross-linked with a bismaleimide (BM) via the DA reaction (Scheme 1) [20]. The resulting product showed mechanical properties similar to those of a conventionally peroxide-cured EPDM rubber with a comparable cross-link density and possessed the added value of recyclability. It was possible to recycle the material via compression molding with excellent conservation of properties.

Alternating, aliphatic polyketones (PK), obtained by copolymerization of carbon monoxide with ethylene and/or propylene, can be modified with FFA to introduce furan groups [21]. The resulting furan-functionalized polyketones (PK-FU) can be thermoreversibly cross-linked with BM (Scheme 1) [22]. Such products can be recycled up to 10 times with hardly any change in performance [21]. The mechanical properties can be modulated by varying the degree of furan functionalization and the furan/maleimide molar ratio [23]. The high brittleness and low impact strength of the PK-FU thermoset were overcome by the addition of a small amount of EPM-FU elastomer as a toughening-agent [24]. Upon the addition of BM, the thermoreversible reaction within and between the phase-separated EPM-FU and PK-FU in the blends (Scheme 1) [24] was shown to significantly increase the impact strength [24]. Since PK is easily functionalized with controlled conversion of furan and forms reversible thermosets when cross-linked with BM [33,35], the resulting blend of EPM-FU and PK-FU is also fully recyclable.



Scheme 1. Grafting of furan groups onto maleated EPM rubber (I) and aliphatic polyketone (II) via reaction with furfurylamine and subsequent (de)cross-linking of the EPM-FU/PK-FU blends via the (retro)Diels Alder reaction with 1,1'-(methylene di-4,1-phenylene)bismaleimide (III).

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