



Macromolecular Nanotechnology

Control of diffusion and exudation of vegetable oils in EPDM copolymers



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ABSTRACT

As a response to environmental problems caused by plasticisers, the feasibility of replacing a significant proportion of the plasticisers in a synthetic ethylene-propylene-diene monomer copolymer (EPDM) matrix with bio-based materials was studied. In that context, different bio-based commercial plasticisers such as Radia® supplied by Oleon, methyl ester of soybean oil, epoxidized methyl ester of soybean oil, methyl oleate, methyl linoleate and untreated vegetable oils (rapeseed, soybean, linseed and tung) were tested. Diffusion analysis using the bi-layers rheology method and exudation analysis highlighted an important exudation phenomenon at 80 °C for all oils tested. To overcome this problem, a second part of this work was focused on the use of a specific highly reactive vegetable tung oil. The *in situ* polymerisation of this oil by thermal activation without the use of catalysts allowed to totally prevent the exudation phenomenon by increasing the viscosity of the oil. Compared with the use of pure tung oil, the degree of exudation was greatly decreased, from more than 8% to less than 1%.

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1. Introduction

Since its introduction on the market in the early 1960s, ethylene propylene diene monomer terpolymer (EPDM) is one of the most important synthetic rubbers. EPDM exhibits excellent heat, ozone, ageing, weathering and chemical resistance being employed in a variety of applications of technical goods such as automotive profiles, building and construction, sealing and fitting systems and even as modifier for thermoplastic materials [1]. Plasticisers allow the processability of EPDM to be enhanced; the maximum amount of plasticiser incorporated into the polymer that does not exude during storage is popularly accepted as the limit of compatibility. Plasticisers can be generally classified as mineral oils, synthetic plasticisers, or vegetable oils and other natural products [2]. Mineral oils are non-polar compounds, classified by their content of aromatic, paraffinic, and naphthenic hydrocarbons. Quantities from 10 to 40 parts per hundred rubber (phr) are often used to soften the rubber and reduce its hardness as well as its elasticity modulus [3]. One major drawback of petroleum-based oils is that they are a non-renewable resource and the aromatic content of some mineral oils may render them carcinogenic [4,5]. Replacing mineral oils with vegetable oils may be a solution to these problems. Unmodified vegetable oils have been used as plasticisers in rubber with different degrees of success [6–12]. Cashew oil was used by Arayapranee et al. [7] in small quantities (1–10 phr) in NR (natural rubber)/EPDM mixtures. However, in their work, they reported conflicting results using this oil. Seed oil was also used in NR and styrene-butadiene rubbers (SBR) by Nandan et al. [13] but only in low quantities

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(2–10 phr) due to poor compatibility with the NR rubber. Alexander et al. [6] used a cardanol at higher proportions (10–50 phr) as plasticisers for carbon black filled NR. Petrovic et al. [11] used soybean oil as a substitute for petroleum oil in NR/SBR rubber. In their work, they studied the possibility of using a cationic polymerisation of the soybean oil [14] that increased its viscosity ten-fold with respect to the untreated oil. These results show interesting possibilities for the use of polymerised soybean oil. In other studies, the oil concentration is relatively low (around 5–10 phr), which is not representative of the use of plasticisers in the elastomer industry. However, vulcanised vegetable oils or factices have a long history of use in the rubber industry. Unsaturated vegetable oils have been used for many years in the elaboration of polymeric materials. Actually, once spread out in a thin layer, some vegetable oils can dry at room temperature by an oxidative process [15,16]. The process involves a reaction of the fatty double bonds with atmospheric dioxygen. Thus, a convenient classification has been developed depending on the drying index, called the “iodine index,” whose value increases with the degree of unsaturation of the oil [17,18]. This ability to naturally crosslink has been known for a very long time, in particular in the field of paint manufacture [19]. Unfortunately, the polymerisation times are very long (several days or weeks). The reaction can be accelerated by the use of thermal polymerisation, which is called the standoil reaction [20]. Oils are first heated at high temperature (greater than 270 °C) in the absence of dioxygen before polymerising by oxidation at room temperature. In this reaction fatty double bonds are thermally polymerised and TAG (triacylglyceride) molecules are crosslinked, leading to an increase in the oil viscosity with the reaction time [21]. The obtained oils are called “standoils.” Many contributions to knowledge about vegetable oil polymerisation have been reported in the last century [22–25]. Among unsaturated vegetable oils, highly reactive tung oil has been extensively applied in industry [26–31]. Tung oil-based polymers [32,33] and tung oil as a reactive diluent [34,35] or modifier [36] have been reported. Tung oil has also been applied as an autonomous repair agent in self-healing epoxy coatings [37], reactive diluents [38] and in UV-curable systems [39]. The tung oil derivatives was used as plasticisers for nitrile rubber for the first time by Placek et al. in 1960 [40]. The results obtained appeared satisfactory, the weight loss was between 0.5 and 2% after aged 48 h at 100 °C for the tung oil derivatives and the hydrogenated tung oil derivatives. All of these studies show the strong interest of the scientific community in this highly reactive vegetable oil in many fields, with the additional aim of finding “green alternatives” to the use of petroleum resources.

In this work, we first studied the plasticiser power of vegetable oils or commercial bio-based oils in an EPDM copolymer. The aim was to simply screen the suitable molecules in terms of their final applications in plasticised EPDM. In the second part of the study, an approach based on the standoil phenomenon was developed to prevent oil exudation. The high reactivity of the tung oil was exploited for its polymerisation at a temperature of around 250 °C under an inert atmosphere (standoil process).

2. Experimental

2.1. Materials and reagents

2.1.1. EPDM matrix

The EPDM used is a Vistalon[®] 8600 (ExxonMobil Chemical) kindly supplied by Hutchinson. The structural formula was defined by ¹H NMR analysis (Fig. 1). The average molar mass values $M_n = 69,000$ g/mol and $M_w = 203,000$ g/mol were measured by size exclusion chromatography. Its density is 870 kg/m³ and its Mooney Viscosity ML (1 + 8 at 125 °C) is 81MU based on test ASTM D1646. The solubility parameters obtained by chemical method [41] are $\delta_D = 18.29$ MPa^{1/2}, $\delta_P = 1.91$ MPa^{1/2}, and $\delta_H = 2.03$ MPa^{1/2} resulting in a global solubility parameter $\delta_{tot} = 18.5$ MPa^{1/2} and a radius of interaction of 7.2.

2.1.2. Mineral and vegetable oils

A mineral oil (Torilis[®] 7200, TotalFina-Elf, France) was used as a reference for oil plasticiser into the Vistalon 8600 to mimic industrial compositions. The specific gravity of this oil is 0.90 g·cm⁻³ at 20 °C.

A selection of vegetable and industrial oils was used (Tables 1 and 2). The commercial Radia[®] oils were supplied by the Oleon Company, the mineral oil by the Hutchinson Company and the vegetable oils were ordered from Sigma-Aldrich and Oleon. The fatty acid composition of the vegetable oils was defined by ¹H NMR (for example, see the ¹H NMR spectrum of the

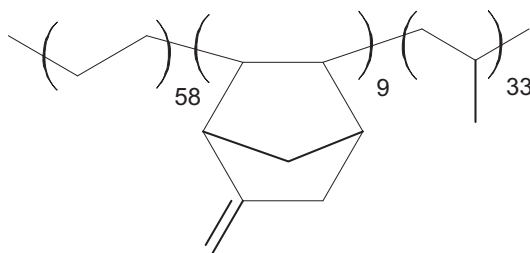


Fig. 1. EPDM Vistalon[®] 8600 structural formula with the mass percent of each repeat unit.

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