



Interrelationship between total volatile organic compounds emissions, structure and properties of natural rubber/polycaprolactone bio-blends cross-linked with peroxides



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ARTICLE INFO

Article history:

Received 28 January 2017

Received in revised form

3 April 2017

Accepted 7 April 2017

Available online 28 April 2017

Keywords:

Natural rubber/polycaprolactone blends

Peroxide curing

Volatile organic compounds

Structure-property relationships

ABSTRACT

Natural rubber/polycaprolactone (NR/PCL) bio-based blends with different organic peroxides were prepared using an internal batch mixer and subsequently cross-linked at 170 °C. Two types of commonly used organic peroxides, dicumyl peroxide and di(tert-butylperoxyisopropyl)benzene peroxide, were applied as free-radical initiator. Cross-linking efficiency of NR/PCL blends were investigated using oscillating disc rheometer measurements, followed by infrared spectroscopy, thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis and tensile testing. Total volatile organic compounds (TVOCs) emissions were determined using headspace analysis integrated with gas chromatography with flame ionization detector. Determined TVOCs emissions varying in range 21.6–52.1 µg/g and generally value of this parameter decreased with increasing content of PCL phase in studied blends or with application of more efficient di(tert-butylperoxyisopropyl)benzene peroxide as cross-linking agent. It was found that increasing of TVOCs parameter indicated deterioration of mechanical properties of NR/PCL blends, which corresponded with the changes in chemical structure and thermal properties of cross-linked NR/PCL. This confirms that evaluation of TVOCs parameter is interesting alternative for “conventional methods” to characterization of the studied bio-based blends.

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1. Introduction

Dynamic development in the field of bio-based polymers and composites result in their widespread applications in different branch of industry, such as eco-friendly package, medical, automotive, engineering, etc. [1–3]. Estimated data shown that in 2016 the global production of biodegradable polymers exceeded 760 thousand tonnes, while production of non-biodegradable polymers

from natural resources was around 1300 thousand tonnes. Furthermore, the prediction is that in 2019 the total global production capacity of biodegradable and non-biodegradable polymers from natural resources will increase almost four times [4]. This trend is due to economic and environmental factors, which are related to limited petroleum resources, continuously increasing amount of polymeric wastes and higher awareness of the society. As a consequence, searching for novel biodegradable polymeric materials with tailored properties and suitable price is currently a subject of interest in many research groups around the world [5–7].

Preparation of bio-based polymer blends and composites via melt-compounding is a commonly applied method to fabricate new materials based on commercially available components [8]. However, physical blending defined as simple mixing in the melt state without any chemical reactions between components, usually affect the weak interfacial adhesion between phases. This results in unsatisfactory performance properties of obtained polymeric materials, which strongly limits their further industrial applications.

Abbreviations: BIB, di(tert-butylperoxyisopropyl)benzene peroxide; CRI, cure rate index; DCP, dicumyl peroxide; DSC, differential scanning calorimetry; DMA, dynamic mechanical analysis; FTIR, Fourier transform infrared spectroscopy; HS-GC-FID, headspace analysis combined with gas chromatography with flame ionization detector; NR, natural rubber; PCL, polycaprolactone; TGA, thermogravimetric analysis; TVOCs, total volatile organic compounds; VOCs, volatile organic compounds.

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Therefore, most of bio-based polymer blends and composites require further compatibilization [9,10]. Among various methods, cross-linking is very promising route for biodegradable polymers modification [11,12] or bio-based polymer blends and composites compatibilization [13,14]. It is well known that free radicals generated during cross-linking resulting in formation of new bonds between polymer chains, while simultaneously some degradation (mainly by main chain scission and oxidation) might occur. Chemical compounds classified as a volatile organic compounds (VOCs) generated during degradation of polymers might affect their performance properties and future applications. However, scientific literature in this field of research is still very limited [15–17]. Detailed information about the correlations between VOCs characteristics and structure-properties of the polymers is very important from environmental and economical point of view, especially in case of biodegradable polymeric materials having direct contact with food [18,19] or tissues [20].

In this work, bio-based NR/PCL blends with variable ratio were melt-compounded and then cross-linked using different type of organic peroxide as free radical initiators. Cross-linking efficiency was evaluated using oscillating disc rheometer measurements. The total volatile organic compounds (TVOCs) emissions from studied samples were investigated using headspace analysis combined with gas chromatography with flame ionization detector (HS-GC-FID technique). Structure and properties of cross-linked NR/PCL blends were determined using an attenuated total reflectance mode Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and mechanical tests (tensile strength, elongation at break, hardness). For a better understanding of interactions between NR and the PCL phase, interrelationship between TVOCs, structure and properties of cross-linked NR/PCL blends were investigated.

2. Experimental

2.1. Materials

Natural rubber (NR) RSS1 with density 0.92 g/cm³ was supplied by Guma-Pomorska (Poland). Polycaprolactone (PCL), Capa™ FB100 with molecular weight of 100,000 g/mol and melting point of 58–60 °C was obtained from Perstorp Holding AB (Sweden). PCL was used due to its good mechanical properties, biodegradability and relatively low processing temperature, which allows for the reduction of energy consumption and prevents degradation of some biopolymers (e.g. polysaccharides or natural rubber) [21]. Two types of commercial available dialkyl peroxides were applied as free-radical initiators during cross-linking of NR/PCL blends. Dicumyl peroxide (DCP) tradename Peroxan DC-P+ having active oxygen assay 5.80%; temperature at which half life time ($t_{1/2}$) is 1 min at 172 °C and di(tert-butylperoxyisopropyl)benzene peroxide (BIB) tradename Peroxan BIB-1 having active oxygen assay 8.98%; temperature at which half life time ($t_{1/2}$) is 1 min at 174 °C were received from Pergan GmbH (Germany).

2.2. Sample preparation

NR/PCL blends were prepared in a GMF 106/2 Brabender batch mixer at 70 °C and rotor speed of 100 rpm. The mixing time equaled 8 min and included 2 min of preliminary plasticization of PCL, 2 min mixing of PCL with NR, and 4 min of mixing the NR/PCL blend with added organic peroxide (DCP or BIB). After compounding in batch mixer obtained blends were homogenized on laboratory two roll mills from Buzuluk (Czech Republic). NR/PCL blends were cross-linked into 2-mm thick samples at temperature 170 °C and

pressure of 4.9 MPa for the optimal curing time determined according to ISO 3417 standard. Samples of blends were coded as NR/PCL_{X,Y}, where X is NR/PCL weight ratio (90/10 %wt. or 70/30 %wt.) and Y is type of used peroxide (DCP or BIB). For example, NR/PCL_{90/10,DCP} is sample of NR/PCL blend in ratio 90/10 %wt. cross-linked with DCP. The formulations of peroxide cross-linked NR/PCL blends are presented in Table 1.

2.3. Measurements

The curing characteristics was studied according to the standard ISO 3417. The measurements were performed using a Monsanto R100S rheometer (USA) with an oscillating rotor. The rotor oscillation angle was 1°, while torque ranged between 0 and 100 dNm. Cure rate index (CRI) values were calculated in accordance with formula (1) [22]:

$$CRI = \frac{100}{t_{90} - t_2} \quad (1)$$

where: t_{90} – optimum curing time, min; t_2 – scorch time, min.

Chemical structure of cross-linked NR/PCL blends was determined using Fourier transform infrared spectroscopy (FTIR). FTIR spectrophotometric analysis was performed by means of a Nicolet 8700 apparatus from Thermo Electron (USA) equipped with a snap-Gold State II, which allows for making the measurements in the reflection configuration mode. The resolution used was 4 cm⁻¹.

Dynamic mechanical analysis was performed using DMA Q800 TA Instruments apparatus (USA). Samples cut to the dimensions of 40 × 10 × 2 mm were loaded with a variable sinusoidal deformation force in the single cantilever bending mode at the frequency of 1 Hz under the temperature rising rate of 4 °C/min within the temperature range between –80 and 40 °C.

Differential scanning calorimetry (DSC) was performed on a DSC 204 F1 Phoenix Netzsch apparatus (Germany) under nitrogen atmosphere, with gas flow of 20 ml/min, in the temperature range from –80 to 200 °C, and at a heating rate of 10 °C/min. First, 10-mg samples were heated from 30 to 200 °C, then cooled to –80 °C and reheated up to 200 °C.

Degree of crystallinity of PCL phase was determined according to formula (2):

$$X_c = \frac{\Delta H_m}{\Delta H_c \phi} \times 100\% \quad (2)$$

where: X_c - degree of crystallinity (%); ΔH_m - melting enthalpy (J/g); ΔH_c - melting enthalpy at 100% crystallinity, the value of which has been reported to be 136 J/g [23] and ϕ - the weight fraction of PCL phase in the blend.

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 apparatus (Germany). Samples (ca. 5 mg) were placed in a corundum dish. Measurements were conducted in a nitrogen atmosphere for the temperature range 25–550 °C at a heating rate of 20 °C/min.

The tensile strength and elongation at break were estimated in accordance with ISO 37. Tensile tests were performed on a Zwick/Roell Z020 tensile tester (Germany) at a constant speed of 500 mm/min. Direct extension measurements were conducted using an extensometer with sensor arms. Shore hardness type A was estimated using Zwick 3130 durometer (Germany) in accordance with ISO 7619-1. The reported results are the means of 5 measurements per sample.

Swelling degree of NR/PCL blends (0.2 g samples) was determined by equilibrium swelling in toluene (room temperature, 72 h). Swelling degree was calculated in accordance with the

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