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Thermal degradation during melt processing of poly(ethylene oxide), poly(vinylidenefluoride-*co*-hexafluoropropylene) and their blends in the presence of additives, for conducting applications

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Abstract

In this paper, the thermal degradation during compounding of poly(ethylene oxide) and poly(vinylidenefluoride-*co*-hexafluoropropylene) and their immiscible blends was investigated. Infrared spectroscopy, size exclusion chromatography, dynamic rheology, thermogravimetric analysis, and coupled gas chromatography–mass spectroscopy were used. Most of the identified degradation products or substances are glycols, formates, lactones, ethers or even acids for long processing times. The mechanisms for the production of these chemical compounds were already reported in previous publications. Additionally, the influence of carbon black and LiV_3O_8 additives, currently used for enhancing the conductive properties, was studied. Addition of carbon black causes an increase in the PEO stability, whereas addition of LiV_3O_8 has an opposite and dramatic effect. PVDF–HFP is found to be less susceptible to degradation because of the inherent stability of fluorine-containing polymers. However, melt processing provides additional contributions to degradation because of the high viscosities.

Keywords: Poly(ethylene oxide); Poly(vinylidenefluoride) copolymer; Blends; Thermal degradation; Conductive applications

1. Introduction

To obtain plastic materials with improved properties, blending two or more components is now widely applied. Properties of these new materials are combination of their components properties with synergetic effect emerging from special morphologies [1].

Poly(ethylene oxide) (PEO)–poly(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF–HFP) blends are often used in conducting or electrical applications [2–6]. These blends can be obtained in the melt through extrusion, however taking into account the melting temperature of PVDF–HFP, this must be performed at temperatures above 135 °C. In this temperature range, according to the literature [7], PEO undergoes degradation. Thermal degradation of PEO was studied using different experimental methods, such as differential scanning calorimetry [8], thermogravimetry [9], thermal volatilization analysis [10] or dynamic mechanical thermal analysis [11].

Following the work of Costa et al. [12], PEO degradation products seem to emerge in the following way. Hydroperoxide groups –OOH are produced at one of the carbon atoms in the PEO polymer chain by a free

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radical mechanism in presence of oxygen or due to oxygen donors like the PEO molecule itself. This chain may undergo a β_1 scission of the chemical bond between two carbon atoms. As the result of this scission, two shorter polymer chains are obtained: one ending with a methylene radical and the second ending with a formate group. Indeed, methyl formate, 1,2-ethadienol monoformate and 1,2-ethadienol diformate are reported to be produced by this route.

The β_2 scission of the bond between carbon and oxygen leads to a polymer chain ending with an aldehyde group and a molecule of an alcohol is produced. Esters could be produced by cage effect at the hydroperoxide group leading to acidic products with further chain scission. Butyrolactone could be produced by transformation of −OOH groups into −OH [3,5,13].

Carbon black and LiV_3O_8 are commonly used as additives for conducting applications. Indeed, oxygen atoms of the PEO polymer chain attract and interact with both water and ions. Conduction occurs when lithium ions hop or jump from one oxygen atom to another. Such a phenomenon results in travelling of the ions along the chain length [14]. PEO is the leading candidate for the electrolyte in lithium polymer batteries [15,16]. The LiV_3O_8 component is used as a reversible intercalation compound for lithium ions in a lithiated oxide cathode together with lithium salt and polymer. Carbon black was in use as conductive filler since 1950s [15]. This component is added to many polymers, for instance low-density polyethylene (LDPE) [16]. According to Ref. [17], to obtain well conducting polymer material, the minimal loading of carbon black should be from 5 to 35%, depending on the shape of the carbon black particles.

The purpose of this work is to investigate the thermal degradation mechanisms and volatilization products of PEO, PVDF−HFP and their blends in the presence or absence of additives for conducting applications during a melt processing operation.

2. Experimental

2.1. Materials

Two polymers were used in this study: poly(ethylene oxide), PEO produced by Union Carbide and a random copolymer of poly(vinylidenefluoride-*co*-hexafluoropropylene), PVDF−HFP produced by Solvay. Some characteristics of the investigated polymers are given in Table 1.

To investigate the influence of one polymer on the degradation of the second, comprehensive investigations of both neat polymers and their blend with 50% concentration of each of the components were conducted.

Table 1
Characteristics of the polymers

Polymer	M_w (g mol^{-1})	Polydispersity	Melting temperature (°C) (heating rate 10 K/min)
PEO	120 000	6	72
PVDF−HFP	98 000	1.96	132

Carbon black Y 200 was obtained from SN2A with 99.5% of carbon. The density is 1.8 in bulk and 0.20 ± 0.03 in powder. The number average diameter is 35 ± 10 nm. LiV_3O_8 was synthesized by the "Institut des Matériaux de Nantes" (France). It is rod-shaped with a length of 20 μm. To answer for the question of the influence of carbon black and LiV_3O_8 for both polymer degradation processes, measurements on both polymers with these components were performed.

2.2. Blending by solution casting

For reference, blends were obtained by solution casting. Samples containing PVDF−HFP as the only polymer component were obtained by using acetone as solvent. All the other samples were obtained using acetonitrile. The components were blended using magnetic stirring for several hours. In both cases, polymer concentration values in the solution were about 5%. Solutions were dried at the room temperature during several days and after that heated at 50 °C in the aim to remove traces of the solvent.

2.3. Mixing

Samples obtained by blending in the molten state were mixed at 150 °C in an internal mixer (Rheomix 600P Haake) equipped with roller rotors and a chamber with volume of 70 cm^3. The roller speed was set up at 50 rpm. The mixing time values were from 15 up to 60 min. The volatile products of thermooxidative degradation from thermogravimetric analysis were collected in a U-trap at the feed part of the mixer for subsequent analysis. The trap was cooled using liquid nitrogen. Obtained products were identified using GC−MS coupling.

2.4. Infrared spectroscopy

To identify functional groups of degradation products remaining in the samples obtained by the two above described methods for blending, Fourier Transformation Infrared Spectroscopy using ATR mode was carried out on a Nicolet Omni Sampler infrared spectrometer.