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Material Properties

Property correlations for composites based on ethylene propylene diene rubber reinforced with flax fibers

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ABSTRACT

EPDM composites filled with short flax fibers were prepared by melt blending procedure. The effects of fiber loading on the mechanical, thermal and water uptake characteristics were studied. The physico-mechanical, morphological thermal properties and water absorption behavior were discussed using tensile testing, differential scanning calorimetry, thermogravimetrical analysis and scanning electron microscopy. Scanning electron microscopy revealed that the flax fibers were well dispersed in the polymer matrix. The tensile strength and hardness of the composites were found to be improved at higher fiber loading. The water absorption pattern of EPDM/fiber composites at room temperature follows a Fickian behavior for composites with 10, 15 and 20 phr flax fiber.

1. Introduction

Green composites are a specific class of materials, in which at least one of components proceeds from natural resources [1,2]. Among them the natural fiber reinforced polymer composites represent an emerging area in the polymer science because these materials are both environmentally friendly and sustainable [3]. After years of high-tech developments of the synthetic fibers (aramid, glass, carbon, etc), the natural fibers (wood fibers, flax, hemp, jute, sisal, kenaf, ramie and others) have now attracted a renewed interest [4,5]. These natural cellulosic fibers have shown a great potential as substitutes for synthetic fibers, in particular glass fibers, in composites that are extensively used in the automotive and construction industries. Natural fillers as raw materials for polymer reinforcement exhibit many advantages relating to mineral fillers, glass fibers or carbon fibers such as low cost, low density, high specific strength and modulus, ease of fiber surface modification, non abrasion, renewability and biodegradability, good thermal and acoustic insulating properties, recyclability and world wide availability [5–7]. Natural fibers-reinforced green composite materials are utilized in different applications, namely door components, furniture, deck surfaces, window or automotive components [1,8].

However, before to utilize these fiber-reinforced composites into real life applications, especially for massive production, the characteristics of the materials have to be deeply studied to assure that repeatable and reliable results can be obtained. In spite of these obvious advantages, there are several impediments to overcome for using the natural fibers as reinforcements in the composite materials, including lower compatibility between the hydrophobic matrix and hydrophilic fibers, relative high moisture of the fibers, dispersion properties of the resultant composites (uniform dispersion and extreme agglomeration), manufacturing process due to their low thermal stability which limits the applications in engineering thermoplastics. The change in microstructure of these fibers subjected to loading can also significantly affect the final properties of the composites [9–11].

The natural flax fibers are widely used for textiles (linen) and for technical applications, such as specialty papers, composites or insulating materials due to its renewable nature, low cost, easy availability, environmental benefit (i.e. biodegradability), high specific tensile stiffness [8,12,13]. Natural fibers have less impact on

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the health of composite manufacturers because they do not bring about skin irritations, lung cancer [7,14]. Flax fiber is a composite, in which the major constituents are cellulose (around 71%), hemicellulose (around 2.2%), lignin (around 18.6–20.6%) and pectin (around 2.3%) [8,15]. The unidirectional cellulose microfibers constitute reinforcing elements in polymer matrix/cellulosic fiber composite.

It is known that ethylene propylene diene terpolymer (EPDM) is one of the most widely used and fastest growing synthetic rubber [16]. EPDM exhibits remarkable characteristics such as high heat resistance, ozone resistance, low temperature flexibility, cold and moisture resistance to permanent deformation and impact, excellent electrical properties, color stability. EPDM rubber has been widely used in automotive industry as insulation materials for wires and cables, as floor coverings in metro train carriages, joints materials in nuclear plants [17–19]. Even though many interesting papers exist in literature concerning the composites based on polymers and flax fibers [7,8,11,20], a limited research has been conducted on structural characteristics of rubber/flax fiber composites [21–24].

The aim of this paper was to obtain and to investigate the physico-mechanical properties of some EPDM based composites reinforced with flax fibers. Attention has been given to the effects of fiber loading on the final properties of composites. The mechanical and thermal properties, water uptake, rubber-fiber interactions and morphology of the composites were compared.

2. Experimental

2.1. Materials

EPDM monomer (Nordel 4760) was supplied by Dow Chemical Company (Mooney viscosity: 70 ML_{1+4} at 120 °C, 70% ethylene content, 5-ethylidenenorbornene 4.9 wt%, density 0.88 g/cm^3, crystallinity degree 10%). Polyethylene glycol, PEG 4000, was obtained from Advance Petrochemicals LTD (density 1.128 g/cm^3, melting point range 4–8 °C). Irganox 1010 (pentaerythritol tetrakis(3-(3,5 di-*tert*-butyl-4-hydroxyphenyl)propionate) was produced by BASF Schweiz AG (active ingredient 98%, melting point of 40 °C). Dibenzoyl peroxide (Perkadox 14–40B) as vulcanizing agent was supplied by Akzo Nobel Chemicals (density 1.60 g/cm^3, 3.8% active oxygen content, 40% peroxide content, pH 7). Ground flax fiber wastes thread length of max 3 mm were used as reinforcing agent.

2.2. Composite preparation

EPDM rubber/flax fiber composites were obtained by melt blending using a laboratory electrically heated roller mill equipped with a cooling system at a friction ratio 1:1.1 and temperature of 60–80 °C. EPDM (100 parts) was firstly melted 1–2 min, then antioxidant (Irganox 1010) and PEG 400 incorporated and melt-blended (2 min). The mixing was continued until a uniform mixture was obtained. When a uniform mixture was realized, different amounts of ground flax fibers 0, 5, 10, 15 and 20 phr (parts to 100 parts rubber), respectively were introduced (4 min) and then 8 phr of dibenzoyl peroxide as vulcanizing agent was added (1 min). The mixing was continued for another 5 min. The samples were then removed from the roll in form of sheets about 2 mm thick. Test specimens were prepared by compression molding at 160 °C and a pressure of 150 MPa by using an electrical press and then cooled under pressure at room temperature. The compounding recipe is given in Table 1.

Table 1
Composite formulations.

Ingredients (phr)[a]/Code	P0	Pln5	Pln10	Plnl5	Pln20
EPDM	100	100	100	100	100
Flax	0	5	10	15	20
PEG 400	3	3	3	3	3
Irganox1010	1	1	1	1	1
Perkadox 14–40B	8	8	8	8	8
Total	112	117	112	127	132

[a] Parts to 100 parts rubber.

2.3. Measurements

Tensile strength tests were performed with a Schopper strength test machine on dumbbell shaped specimens according to ISO 37/2012. The hardness was determined using a hardness tester according to ISO 7619-1/2011 on samples with thick of 6 mm. The unit of hardness was expresses in ShoreA. The elasticity was estimated with a Schob test instrument on samples of 6 mm thick, according to ISO 4662/2009.

Thermogravimetric analysis (TGA) of the composites was performed on a STA449 F1 Jupiter thermal analyzer (Netzsch, Germany) under nitrogen atmosphere at a heating rate of 10 °C/min. The samples were heated from room temperature to 700 °C at a nitrogen flow rate of 50 ml/min. The onset of degradation temperature, the temperature for which the weight loss is maximum (T_m) and the residual weight were estimated. Differential scanning calorimetry (DSC) measurements were carried out using a DSC200 F3 Maia apparatus (Netzsch, Germany) under nitrogen atmosphere and a heating rate of 10 °C/min from room temperature to 300 °C.

The gel fraction of the crosslinked EPDM/flax fiber composites (with and without flax) was determined by the content of insoluble fraction from crosslinked composite after solvent extraction. The samples were swollen in toluene and extracted after 72 h. The extracted samples were dried in air for 6 days and then in a laboratory over at 80 °C for 3 h to constant weight and finally were reweighed. The gel fraction is given by the relation

$$\text{Gel fraction } (\%) = \frac{m_s}{m_i} \cdot 100 \quad (1)$$

where m_i and m_s are the initial weight and the weight of the insoluble portion of the composite in gel. The crosslink density (ν) of EPDM composites was estimated by equilibrium solvent swelling measurements using the modified Flory-Rehner equation [25]. Pieces of 2 mm thickness (initial weight m_i) were prepared and immersed in toluene for 72 h in order to achieve the equilibrium swelling conditions. Then the swollen sample was taken out from solvent and dried to remove the solvent excess and reweighed (m_g). The traces of solvent were removed by drying in air for six days and in an oven at 80 °C for 3 h. Then the sample was again weighed (m_s). The volume fraction of polymer in the swollen network (ν_{2m}) was calculated from swelling ratio G by the relation:

$$\nu_{2m} = (1 + G)^{-1} \quad (2)$$

With

$$G = \frac{(m_g - m_g)}{m_s} \cdot \frac{\rho_r}{\rho_s} \quad (3)$$

and ρ_r, ρ_s are the densities of EPDM sample and solvent (0.942 g/cm^3 (EPDM) and 0.865 g/cm^3 (toluene)). The densities of EPDM samples were measured by hydrostatic weighing method, according to ISO 2781/2010. The crosslink density was calculated