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Material Properties

Nanocomposite of erucamide-clay applied for the control of friction coefficient in surfaces of LLDPE



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ABSTRACT

The industry of polymeric films has been seeking for practical and economical solutions to obtain high quality polymeric films, which comprises the evaluation of a multitude of parameters, such as mechanical and thermal properties and surface characteristics, among which the friction coefficient (FCO) is of great importance. In this work, LLDPE polymeric films were prepared with the addition of erucamide and commercial organophilic montmorillonite nanoclay Cloisite 20A nanocomposites in the concentrations of 5, 10 and 15%. The films were shaped in a single screw balloon tube extruder, then characterized via Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC), Friction Coefficient (FCO), brightness, opacity and Atomic Force Microscopy (AFM). The results indicated a decrease in and stabilization of the friction coefficient, and allowed an evaluation of the effect of the nanocomposite on the surface of the polymeric films, which involved an increase in brightness and decrease in opacity and roughness.

1. Introduction

In the polymeric film industry, the pursuit of practical and economical solutions for the manufacturing of films is a continuous and necessary process. For the application of such films in packaging, besides the basic demands inherent to each product to be conditioned, the manufacturing processes require special technical characteristics to meet high productivity, endure handling and achieve the final shape.

During industrial production, an interaction between the products can occur, reducing the material's efficiency through factors connected to its chemical and physical structures. Several parameters must be evaluated in order to achieve high quality polymeric films, such as mechanical and thermal properties and surface characteristics, especially the friction coefficient (FCO). Polymeric films tend to adhere to other surfaces when in contact, hampering the production process.

The growing demand for polymeric products directed to innovative applications incites a great interest in producing surfaces that are more resistant and have fewer imperfections. According to Mansha et al. [1], the resistance of a material is related to a decrease in its friction coefficient. Additionally, Rabello [2] believes that correlate additives such as slide additives can help decrease this coefficient, as well as the abrasion caused either by the adhesion between materials or by other factors during the production process. As reported by I.A.P [3], the thin coating obtained after the application of slide additives reduces blockage and friction between the materials, along with their friction coefficients.

Additives are usually blended in polymeric films, despite their strong tendency to migrate to the film's surface, which hampers industrial manipulation. The slide additives more often employed are fatty acid amides, which, due to their incompatibility with most polymers, migrate to the surface, forming a crystalline structure that reduces the FCO. Erucamide and oleamide are the additives most frequently used [4].

Erucamides rapidly diffuse in the polymeric matrixes, enabling the definition of the FCO on the surface according to the percentage applied in the formulations. The migration of erucamide molecules to the polymer's surface is fast, reaching equilibrium in less than 24 h, with an established value of 0.35 for the FCO of the polymeric films during that period [5]. However, due to the high mobility of the erucamide molecules on the surface of products, FCO values shift rapidly, with the risk of generating negative consequences during the manufacturing stages of packaging and plates, or even during the subsequent applications of

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the polymers [6]. The migration speed of slide additives is associated with the temperature, the mobility of the molecules in the polymeric matrix and the concentration of the additive. According to Schouterden et al. [7], both mobility and the speed of migration to the surface are related to the difference in polarity between the molecules constituting the additives and the molecules in the polymeric matrixes. In the industry, FCO values of the polymeric surfaces are adjusted by controlling the percentage of these additives that is incorporated and considering the type of polymeric matrix.

The problems related to FCO can occasion production downtime for the adjustment of the variables in the process during the trimming, impression and welding operations, leading to significant losses in productivity and energy consumption and, consequently, reducing the quality of the final product. Schwope et al. [8] showed that antioxidizing and slide additives migrate more quickly when constituted of smaller and more volatile molecules. According to Eniko [9], the mobility of the additives is detached from the type of polymer and crystal size, depending instead on the magnitude of the fraction of free volume in the non-crystalline stage. Thus, controlling FCO values is essential to the production process of polymeric films.

Erucamides are fatty acid amides which are incompatible with most polymers. The difference in polarity hampers homogenization and distribution of erucamides along the polymeric surface, although its migration to the surface is fast. The mobility of erucamides is due to the presence of polar functional groups in its chemical structure. The migration mechanisms depend on the average size and the interactions between the functional groups and the polymeric molecules. These characteristics define an effective diffusion coefficient for the erucamide molecules and establish the diffusion rate in the polymeric materials [2].

One way of interfering in the mobility of the erucamide molecules is to alter their polarity and effective average size and, consequently, their effective diffusion coefficient in the polymeric matrix. However, this interference must occur through a physical process, thus not jeopardizing the chemical structure and the effectiveness of the erucamide molecules [10]. The shift in effective average size, as well as the modification of the erucamide molecules' polarity, can be reached with the aid of interspersed nanoclays, resulting in a nanocomposite with bigger size and mass. The nanoclays are anchored to the sites of the erucamide molecules, hampering their migration when applied in polymeric matrixes [10]. The interspersion of the erucamide molecules in nanoclays is a process that can provide different values for the binding energy, modifying the migration characteristics of the slide agent through the polymeric matrix.

In this context, this work had as a main objective the attainment of an erucamide, nanoclay and polyethylene nanocomposite to act as a compatibility agent with a controlled form in the diffusion mechanism for controlling the FCO. The nanoclay employed was montmorillonite, organofilized via the ion exchange of the cathodes present in the lamellas for organic cathodes. The organofilization provides an expansion between the channels of the material, making the clay more compatible with polymers.

Subsequently, the changes in the effective size of the erucamide molecules was evaluated, along with the binding energy with the molecules of the polymeric matrix after the controlled interspersion process between the erucamide molecules and the clay nanoparticles. The nanocomposites were attained with different characteristic, aiming to increase their capacity for positively interfering with the migration mechanisms of the slide agent in polymeric materials. Such changes in a controlled way allowed the establishment of values for the effective diffusion coefficient for the nanocomposite, as well as a control in the migration rate of the slide agent in the polymeric matrixes and an adjustment on the FCO values of the polymeric surfaces in pre-determined times.

According to Alves [11], the presence of erucamide significantly increases the interplanar distance of the clay. Therefore, the nanoclay

containing interspersed erucamide is expected to act as a compatibility agent between the polar molecules of the erucamide and the apolar molecules of linear low-density polyethylene, minimizing the migration of the erucamide molecules and making the FCO more uniform and stable on the surface.

2. Materials and methods

The materials employed were industrial erucamide with 99% of purity (CRODA), Cloisite 20A montmorillonite (Bun Tech), low-density polyethylene (LDPE, Braskem) and linear low-density polyethylene (LLDPE, Braskem).

The methodology applied for conducting this research consisted in several stages. Initially, a method was evaluated for the interspersion of the erucamide molecules in the structure of the montmorillonite nanoclay (20A) through the treatment of the nanoclay in an erucamide solution. According to Silvano [12], the results for such treatment showed the possible interspersion of erucamide in nanoclay, presenting increases in the basal spacing.

The subsequent stage of this research involved the preparation of a master compound from the nanoclay-erucamide nanocomposites, incorporating the LDPE via a single screw extrusion system with a temperature profile in the four heating zones, 180, 170, 160 and 145 °C, respectively. For the preparation of the masters by interspersion on the melted state, a limit percentage of 1% of erucamide was used, since in higher proportion the erucamide would hamper the extrusion process. The pellets obtained from the compound were called masterbatch of LDPE/MMT-EU.

For the production of the LLDPE films, the material was vertically extruded through a ring-shaped matrix, in which an air blast was constantly blown, expanding the material into a balloon-like shape. The extruder employed was a single screw balloon tube extruder, from Oryzon, with 7 heating zones; it was used, respectively, in the temperatures of 185, 185, 185, 185, 185, 190 and 205 °C, with a rotation of 93 rpm and pre-established parameters and process variables. The film was molded by tubes located above the matrix, and subsequently spooled.

The LLDPE films were produced with the enhancing of the master compound LDPE/MMT-EU. In accordance with the literature, the average value of 2500 ppm (0.25%) was established for the erucamide added in the film to obtain low FCO values; posteriorly, films with 600 and 1250 ppm were also produced. The mass percentages of the master compounds in relation to the LLDPE polymeric matrix were established according to Table 1. The erucamide percentages were fixed using samples of virgin LLDPE, LLDPE with erucamide and LLDPE with nanoclay as references to evaluate the influence of these compounds in the final properties of the films. For the tests to be conducted, 300 g of each concentration of the material were produced.

Characterization of the erucamide-nanoclay nanocomposites (ERU-MMT) and evaluation of the surface properties of the LLDPE films.

The Transmission Electron Microscopy (TEM) technique was

Table 1
Films with different concentrations of the erucamide/nanoclay nanocomposites.

Sample	PEBDL (g)	Mix (PEBD/ERU/20A)	Erucamide (g)	Nanoclay 20A (g)
0	299,25	75 g ERU	75	0
1	299,25	80 g PEBD/ERU/20A (5%)	75	5
2	299,25	80 g PEBD/ERU/20A (5%)	75	5
3	299,25	84 g PEBD/ERU/20A (10%)	75	10
4	299,25	84 g PEBD/ERU/20A	75	10
5	299,25	84 g PEBD/ERU/20A	75	10
6	299,25	89 g PEBD/ERU/20A	75	15
7	299,25	89 g PEBD/ERU/20A	75	15
8	299,25	75 g 20A	0	75

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