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INVESTIGATION OF THE USAGE OF hBN IN THE WORKABILITY OF LINEAR LOWDENSITY POLYETHYLENE

HBN'NİN LİNEER DÜŞÜK YOĞUNLUKLU POLİETİLENİN İŞLENEBİLİRLİĞİNDE KULLANIMININ İNCELENMESİ

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ABSTRACT

Improving the properties of plastics has always been a curious research topic in the scientific and industrial field, aiming to replace engineering plastics with cost-effective plastics for engineering applications. Looking at the past, there are studies to improve the mechanical properties of the plastics used and to add various properties. The usage areas of BN, which has an important potential today, such as high thermal conductivity, electrical insulation, chemical stability and easy workability, have found a place in many industrial applications as a result of recent researches. In addition to these, it is known that it is used as a process aid in the polymer industry. The main task of the process aids is to reduce the shear stress of the melt by covering the die mouth during extrusion due to low surface tensions. In this way, it reduces the pressure in the mold mouth and eliminates surface defects called melt fractures. In addition to this feature, the use of hexagonal boron nitride (hBN) as an additive in the preparation of masterbacths and the production of a new material and its effect on the processability of linear low density polyethylene were investigated. Accordingly, in this study, a masterbatch form was prepared with hBN-LLDPE, and then analytical and spectroscopic characterization of this material was carried out. As a result of the analyzes made, it was seen that hBN is a good processing aid and the masterbatch formed with 5% additive exhibited the best mechanical properties

Keywords: h-BN, polyethylene, masterbatch

ÖZET

Plastiklerin özelliklerinin iyileştirilmesi, mühendislik uygulamaları için mühendislik plastiklerini uygun maliyetli plastiklerle değiştirmeyi amaçlayan bilimsel ve endüstriyel alanda her zaman merak edilen bir araştırma konusu olmuştur. Geçmiş dönemlere bakıldığında, kullanılan plastiklerin mekanik özelliklerini geliştirmek ve çeşitli özellikleri eklemek için çalışmalar bulunmaktadır. Günümüzde önemli bir potansiyele sahip olan refrakter özelliği yüksek ısı iletkenliği, elektriksel yalıtkanlık, kimyasal kararlılık ve kolay işlenebilirlik gibi üstün özellikleri olan BN' nin kullanım alanları, son zamanlarda yapılan araştırmalar sonucunda pek çok sanayi uygulamasında kendine yer bulmuştur. Bunların yanı sıra polimer sektöründe de proses yardımcısı olarak kullanıldığı bilinmektedir. Proses yardımcılarının esas görevi düşük yüzey gerilimlerinden dolayı ekstrüzyon sırasında kalıp ağzını kaplayarak eriyiğin kayma gerilimini azaltmaktadır. Bu sayede kalıp ağzında meydana gelen basıncı azaltarak, eriyik kırığı olarak adlandırılan yüzey kusurlarını ortadan kaldırmaktadır. Bu özelliğinin yanı sıra hegzagonal bor nitrür (hBN), master

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bacthlerinin hazırlanmasında katkı maddesi olarak kullanımı ile yeni bir malzeme üretimi ile polietilenin işlenebilirliğine olan etkisi araştırılmıştır. Bunlara bağlı olarak bu çalışmada önce hBN' doğrusal düşük yoğunluklu polietilen ile masterbatch formu hazırlandı daha sonra bu malzemenin analitik ve spektroskopik karakterizasyonu gerçekleştirilmiştir. Yapılan analizler sonucu hBN'nin iyi bir işlem yardımcısı olduğu %5'lik katkıyla oluşturulan masterbatchin en iyi mekanik özellikler sergilediği görülmüştür.

Anahtar Kelimeler: h-BN, polietilen, masterbatch

INTRODUCTION

Products made of polymer and polymer-derived materials have become an indispensable part of our lives. It is possible to come across the use of plastic materials in almost every device, equipment and goods we use today. Kitchenware, electronics, stationery, cars, computers, mobile phones etc. It is also used extensively in the healthcare industry. It is enriched with various additives to give these polymers many different and superior properties, such as UV resistance, strength, flexibility, clarity, gloss, and thermal resistance, according to their areas of use. In addition, such additives are also used to eliminate flow instabilities that may occur during the extrusion stage.

Flow instabilities occur in many commercial polymer processing operations, including profile extrusion, film casting, film blowing, and blow molding (Petrie et al., 1976; Ramamurthy,1986). In this study, it is aimed to investigate hBN, which has many superior properties, in terms of removing surface defects and increasing production efficiency, as well as serving as a lubricant in the processing of polyolefins, which are known for their superior properties. It has been shown that certain boron nitride based compositions can act as effective processing aids in the extrusion of a range of fluoropolymers and polyolefins (Rosenbaum et al., 1995). Boron nitride can be used successfully as machining aids not only to eliminate sharkskin melt fracture but also to greatly delay it to significantly higher shear rates in the gross melt fracture region. Conventional fluoroelastomers are known to eliminate only surface melt fractures.

The linear macromolecular structures of the polymers are very large and it is known that they consist of rigid segments that provide the flexibility of the molecular chains gained by the rotation ability, which is the main feature of the polymer structure. Another property of polymers is that strong chemical forces bind to a polymer chain, while intermolecular forces bind chains that are significantly weaker. The possibility of modifying the structural properties of polymers over a wide range provides various tribological applications of polymers and polymer composites. The application of different fillers gives an opportunity to improve the tribological behavior of polymers (Hubáček et al., 1997).

Extrusion is the most important and largest technology in the polymer processing industry. LLDPE, which is a type of polymer used in this industry, has better appearance properties, lower production-recycling costs, as well as high chemical resistance and good mechanical properties in many areas such as food packaging, stretch film, lids, buckets, cable coatings and cosmetics preferred because it is widely used. These processes are applied for most polymeric materials and mostly extrusion is used for these processes. Extruders have several important functions, such as transporting polymers (from a hopper to a die), polymer melting, pressure building, mixing materials for thermomechanical and chemical homogenization, and finally product forming. Melting should be rapid to provide enough room for good material mixing. Melting and mixing is fundamental in polymer processing and is crucial for material recycling of new, advanced materials, polymer composites or polymer blends, as well as plastics (Kazaktchkov et al., 2002).

MATERIAL AND METHOD

In this study; boric acid and urea were refluxed at 1:2 effluent concentration, in ethyl alcohol medium, using a closed system for 3 hours. Then, the powder obtained by filtration was dried in an oven at 80 °C. For the calcination process, four different temperatures (800, 900, 1000, 1100 °C) were pyrolyzed in nitrogen atmosphere for 16 hours and calcined in air atmosphere at 600 °C for 2 hours. Since the obtained hBN derivative is a synthesis product, some compounds that do not react and exist as by-products form impurities. The removal of these impurities is also a very important parameter in determining the effectiveness of hBN as an additive agent. For this purpose, thermal purification method was used to obtain hBN derivatives with high impurity. Since hBN derivatives will reach the highest impurity value at the pre-oxidation temperature, they were heated up to this temperature in an air atmosphere. The oxidation temperature of the synthesized hBN derivatives was determined by TGA analysis, and each hBN derivative was purified in an air atmosphere at a heating rate of °10C/min in a laboratory-type camera heater, up to the oxidation degree obtained as a result of TGA analysis, and it was recorded. The findings are discussed in the conclusion and evaluation part.

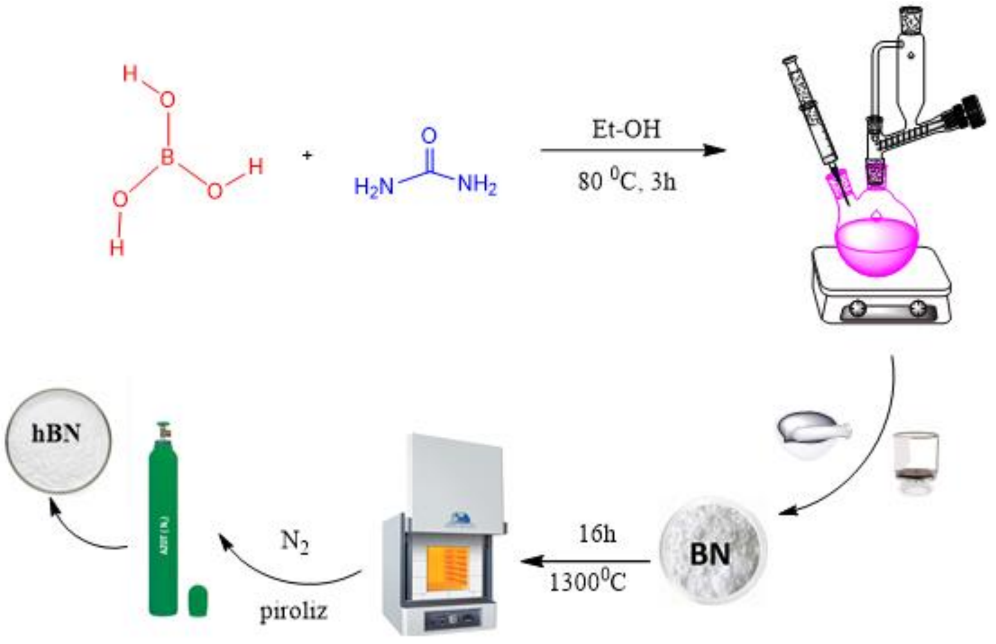

Figure.1. HBN Synthesis and Purification Steps

Bringing additives in powder form to masterbatch form enables a more accurate evaluation of their effects. In the preparation of masterbatches, an automatic dosing, twin screw co-rotate laboratory type extruder was used (L/D: 48, screw diameter: 58 mm). Extruder operating temperatures for LLDPE are between 170-190 °C.

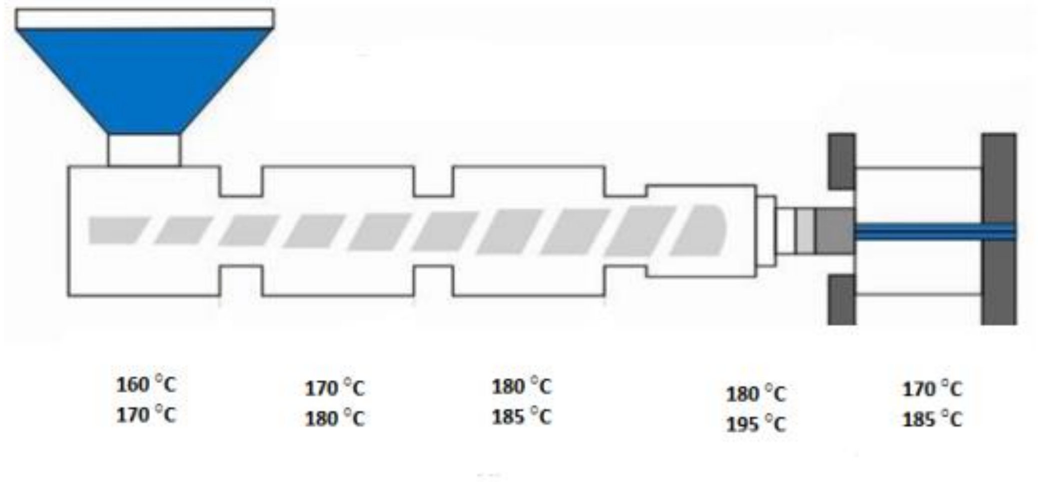

Figure 2. Extruder Operating Temperatures

Masterbatch forms with 95% LLDPE carrier were prepared at 5% concentration of hBN derivative. The most important point to be considered while preparing the masterbatch is that the additive is dispersed in the polymer matrix without agglomerate. In order to ensure the dispersion of hBN in the polymer matrix, a dispersion agent was produced using 1%, 5% hBN and 94% LLDPE carrier masterbatch. In order to ensure the compatibility of hBN and polymer matrix, the maleic anhydride-based complex that we synthesized before, 1% hBN as compatibilizer, and

94% LLDPE carrier masterbatch was produced. LLDPE masterbatch containing 5% commercial nucleating agent was used for comparison. The MFI value of the carrier polymer used is 190 °C, 2.16 kg/10 min for LLDPE.

In this study, masterbatches of purified hexagonal boron nitride with LLDPE in two different compatibilizers were prepared. Bringing additives in powder form to masterbatch form enables a more accurate evaluation of their effects. In the preparation of masterbatches, an automatic dosing, twin screw co-rotate laboratory type extruder was used (L/D: 48, screw diameter: 58 mm). Extruder operating temperatures for LLDPE are between 170-190 °C.

Table 1. Synthesized Materials and Codes

			Product Content			
Product Codes	**Base Polymer**	**%**	**Additive Material**	**%**	**Compatibilizer**	**%**
A1	**PE**	%99	**h-BN**	%1	**Commercial**	%1
A2	**PE**	%95	**h-BN**	%5	**Ca-Ma**	%1

Within the scope of the study, firstly, chemically pre-purified hexagonal boron nitride and the compatibilizing agents BYK and Ca-Ma masterbatch were dosed gravimetrically as an additive to the LLDPE plastic polymer in the laboratories of KSU, ÜSKİM and Faculty of Forestry in order to carry out preliminary studies. At this stage, the extruder speed was set as 40 rpm, the temperature of the 1st zone was set as 175 °C, the 2nd zone 180 °C, the 3rd zone 180 °C, the 4th zone 185 °C and the 5th zone 190 °C, and the prepared mixture was fed into the extruder. After the new materials produced are cooled in the cold water pool at the exit of the extruder, they are taken to the crusher and the material production is completed. In the next step, the added polymers produced and broken were dried in an oven at 105 °C for 24 hours, and the production phase was completed. The masterbatches obtained were tested on the blow film extrusion line of KOREN Chemistry and blow film production was carried out.

RESULT AND DISCUSSION

The resulting hBN, masterbatch and the final product blow film were characterized by various techniques. First of all, Perkin Elmer brand Fourier transform infrared spectrophotometer was used to determine the chemical bond vibrations of the synthesized hBN (Figure 3). The presence of oxygen-bearing functional groups in pure h-BN is evident from the FTIR spectra of hBN. Apart from the characteristic peak of B–N, peaks corresponding to B–N–O are observed at 1173 cm^{-1} and 947 cm^{-1}. The peak at 1112 cm^{-1} corresponds to B–O–H in plane bending. The FTIR spectrum of hBN shows very intense B-N peaks prominent at 1386 cm^{-1}, which can overlap with other vibrations. The presence of the functional group at 2950 cm^{-1}, which corresponds to the hBN -CH stretch, is attributed to the hemiacetal junction in hBN. In the –OH stretching frequency in the structure of hBN, the red shift also indicates covalent bonding due to hemiacetal formation (Gulmine et al., 2002; Wu Jingli et al., 2014).

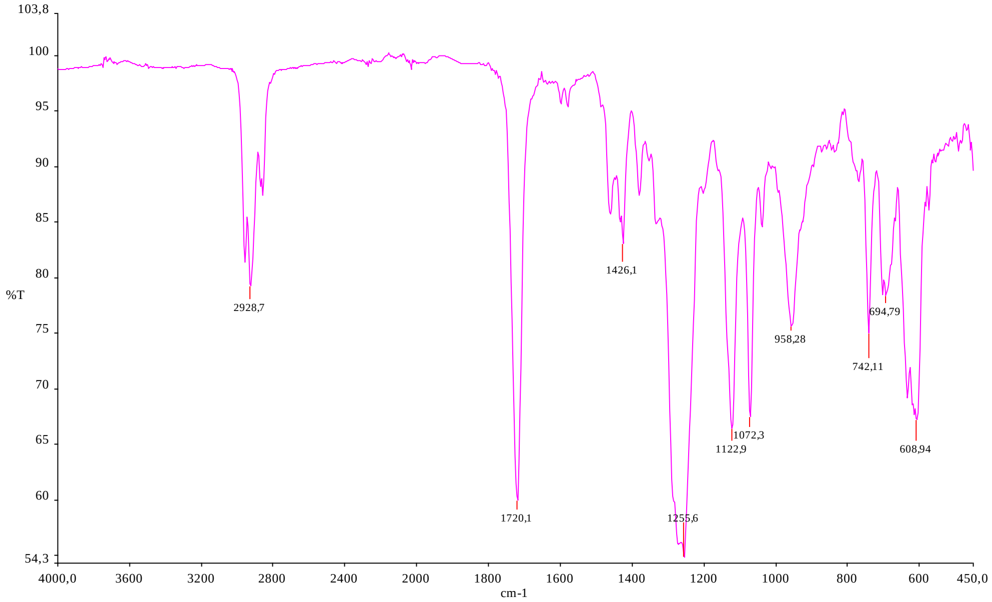

Figure 3. LLDPE/ Hbn of F-TIR Spectrum

A number of analyzes were carried out on the blow films obtained. First of all, thermogravimetric analyzes were carried out to obtain information about the physical transitions of the blow film. In this context, differential scanning calorimetry (DSC), heat treatment was applied from room temperature to 220 °C in 10° increments per minute, and the answers given were recorded. As seen in Figure 4, a glassy transition point of 0.2615 mW was observed between 63.7-70.3 °C. The melting point was then found at 217 °C. The reason why LLDPE differs from its characteristic melting point is that it contains hBN and compatibilizing agents (Majewsky et al., 2016; Reyes Labarta et al., 2006).

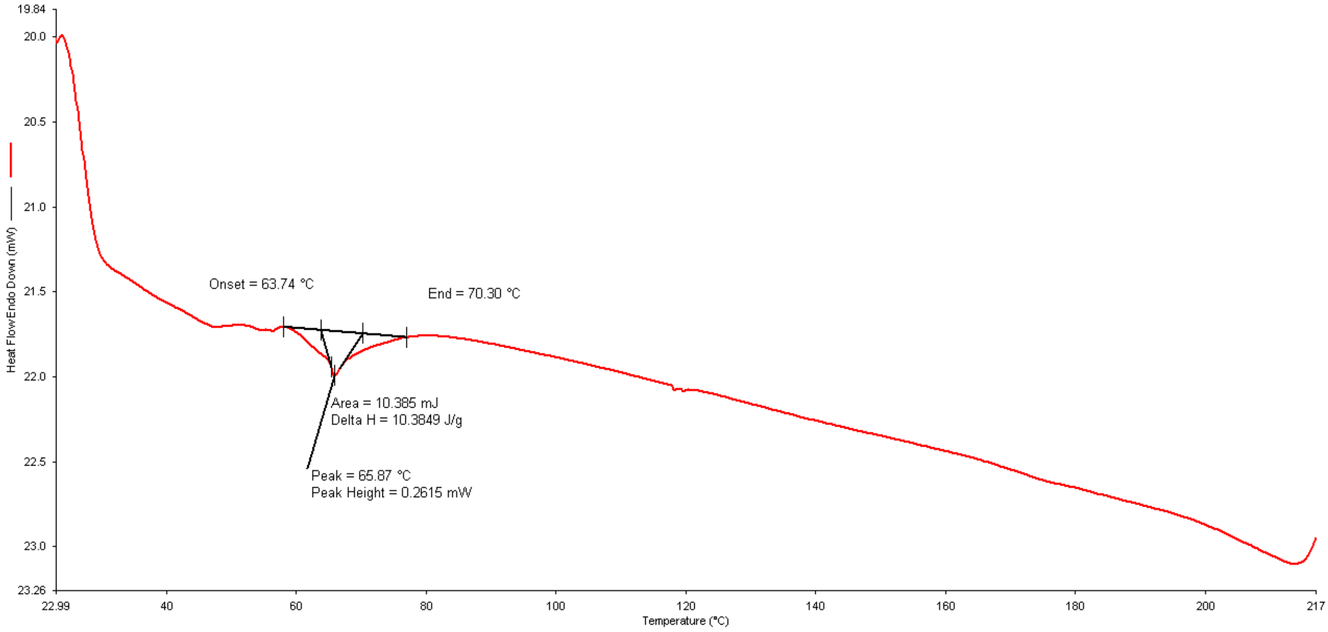

Figure 4. LLDPE/HBN Of DSC Thermogram

Thanks to thermogravimetric analysis, which is another characterization, the answers given by applying heat treatment to the blow film in increments of 5° per minute up to 600 °C were recorded. Looking at the thermogram obtained in Figure 5, it is seen that there are two different mass loss regions. First, there is a mass loss of 78% in the range of 240-320 °C. This loss refers to the breaking of the C-C bonds in the polyethylene chain. The second mass loss region shows that the ring structure of hBN opens at 14 percent between 412-547 °C.

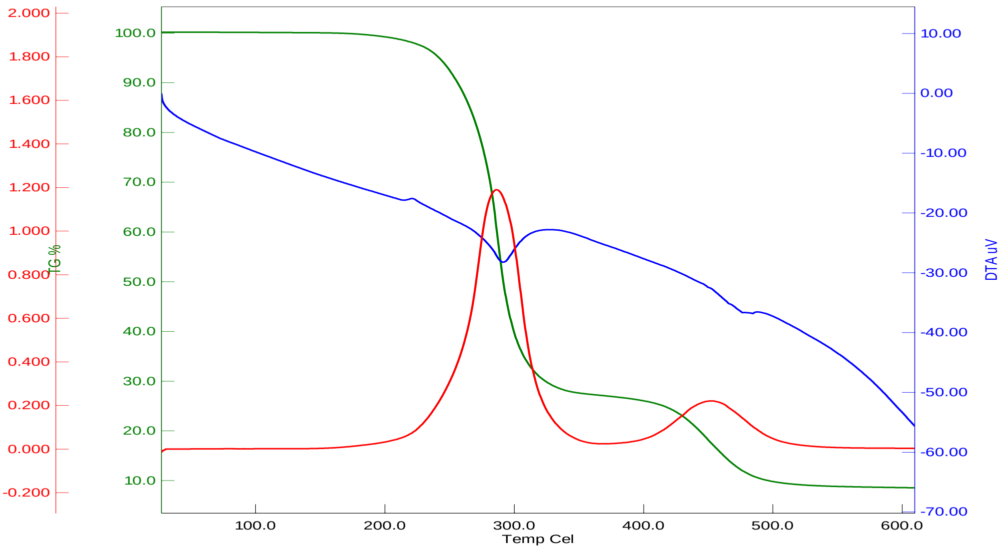

Figure 5. LLDPE /H-BN DSC Chart

The mechanical properties of LLDPE/hBN blow film were evaluated at an injection rate of 3 inches/s using tensile and impact test materials. Tensile tests were recorded on the Instron 5567 device with an expansion value of 3 inches per minute and a loading of 10 kN. It was studied in three repetitions. Impact tests of blow film were performed with ASTM D256 method. The samples were notched with a thickness of 0.9 mm at a 45° angle. A weight of about 2.2kg was used for raw PE and 1kg for blow film. Impact energy was recorded as ft-lbs/in. In Figure 6, the modulus of PE increased by 1% with the addition of 1% hBN. The increase in this value can be attributed to the strengthening of the material, providing a reinforcing effect for the LLDPE chain of hBN. It also has a higher tensile modulus compared to hBN/LLDPE (Gibert et al., 2000; Wong & Lam, 2002).

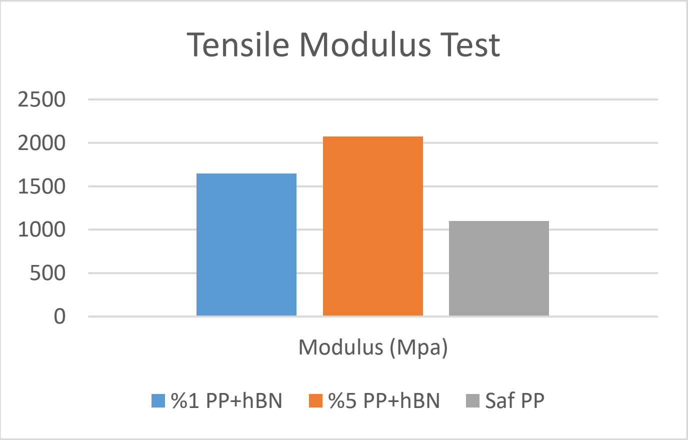

Figure 6. Tensile Modulus Test

In the characterization studies, it is seen that hexagonal boron nitride was synthesized successfully and with high purity. In the strength tests performed on the blow film, which is the final material obtained, it is seen that the hBN added LLDPE is 48% better. In this way, the product both gained strength and reduced the extruder head pressure during production, improving the performance and tensile values of the device. Moreover, it increased the gross melt fracture (GMF) values, which is the surface defect that occurs at high shrinkage ratios, to higher values. There is a serious potential in its use as an alternative material, especially in industrial areas (Arunvisut et al., 2007). The next study will continue with different compatibilizers and different polymers.

CONCLUSION

Fluorine-based processing aids used in the processing of polyolefins have some fundamental problems. These can create fluorinated gases that are particularly harmful to the ozone layer and the environment. The production of these materials is costly and the unit prices are quite high. During extrusion, fluorine-based additives adhere to the die mouth outlet and especially to the screw surface. This adhesion creates serious costs for adhesion under temperature and cleaning in product changes. Another disadvantage is that they have a highly hydrophobic structure, causing static electricity to be charged during product processing and in the final product. Gases from fluorine-based additives that decompose during extrusion are toxic and pose a potential cancer hazard. On the other hand, it also reduces its effectiveness in the use of different filled polymers. These products are generally imported. h-BN, which has a unique crystal structure that we use in the processing of polyolefins, is an environmentally friendly material. The fleece structure showed an antistatic effect in the final product. During the extrusion, there was no clinging or sticking on the screw inside the mold mouth and the sleeve. In this way, the cost of cleaning is eliminated. It does not release harmful gases due to its high thermal stability at extrusion temperature. High purity h-BN synthesis was performed and characterizations were carried out, and it was demonstrated as a result of the tests that it provided 33-35% increase in efficiency in the processing of polyolefins, reduced energy consumption by reducing the current values by 5-7% during extrusion, and eliminated surface defects. We expect that the use of 1% and 5% masterbatches will reduce static, especially in blown film and injection molding products, and the appearance of the products will be smoother and brighter.

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