

PREPARATION AND TENSILE STRENGTH TESTING OF NANOCRYSTALLINE ZIRCONIUM OXIDE - POLYETHYLENE COMPOSITES

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الملخص

ينتج عن إضافة المواد المائنة النانومترية غير العضوية إلى البوليمرات أصناف جديدة من المواد المركبة التي تجمع بين خواص الحبيبات النانومترية من قوة ميكانيكية ومعامل مرونة عالي وثبات حراري، وخواص البوليمر الذي يمتاز بسهولة التشكيل والمرونة. دفع هذا الاستنتاج إلى إجراء بحث تضمن مزج مسحوق من الزركونيا النانومترية بمتوسط حجم حبيبي قدره حوالي 28 نانومتر وبنسب وزنيه تتراوح بين 0 % إلى 12 % مع البوليثين عالي الكثافة. أجريت عملية كبس لهذه الخلطات المركبة من النانوزركونيا والبوليثين عند درجة حرارة 170 درجة مئوية ولمدة 3 دقائق لغرض الحصول على صفائح من مادة مركبة. تم تعريض هذه الصفائح لاختبار الشد الميكانيكي وفحص للبنية المجهرية باستخدام مجهر المسح الإلكتروني لتقييم مدى انتشار حبيبات النانوزركونيا خلال المادة البوليمرية.

أظهرت النتائج المتحصل عليها انخفاض في مقاومة الشد القصوى مع زيادة محتوى النانوزركونيا وهذا يمكن أن يكون راجع إلى الزيادة في الحجم الحر (Free volume) وإضعاف قوة الترابط بين جزيئات البوليمر. أوضح الفحص المجهرية انتشار حبيبات النانوزركونيا بشكل جيد خلال البوليمر بالنسبة للعينات المحتوية على 12% نانوزركونيا.

ABSTRACT

Addition of nanocrystalline inorganic fillers to polymeric materials represent a new class of materials which combine the properties of inorganic particles (mechanical strength, modulus, thermal stability) with ease of processing and the flexibility of the organic polymer matrix. This has prompted the present work which involved blending nanocrystalline zirconium oxide, zirconia, powder of an overall average particle size of about 28 nm with high density polyethylene (HDPE) and then hot pressed at 170°C for 3 minutes to produce composite sheets. The weight percentage of nanozirconia in the composite was varied from 0 to 12%. The composite sheets were subjected to tensile testing and scanning electron microscopy (SEM) to assess the degree of dispersion of nanozirconia particles within the polymer matrix.

The results obtained showed that the maximum tensile strength decreased with an increase in the nanozirconia content. This may be due to a consequent increase in free volume and lowering of the interaction between the polymer molecules.

SEM investigation showed the nanozirconia particles to be dispersed within the polyethylene matrix to a fairly good extent for the composite specimen containing 12 % nanozirconia.

KEY WORDS: Nanocrystalline; Polymeric materials; Zirconium oxide; Zirconia;
High density polyethylene; Nanocomposites

INTRODUCTION

The addition of inorganic spherical nanoparticles, particles with diameters below 100 nm, to polymers allows the modification of the polymers physical properties as well as the implementation of new features in the polymer matrix. Decreasing the particle size leads to an increase in the surface/ volume ratio, so that surface properties become crucial [1].

The main effect of rigid fillers is to increase the elastic modulus of a polymeric composite. The important factors in determining the modulus are the concentration of the filler, shape and size of particles, relative modulus of the components, and the manner in which the particles pack. Generally, the nature of the interface, except for its effect on particle packing, and the adhesion degree are not very important factors in obtaining the elastic modulus, but they are very important in determining the strength and stress – strain behaviour of composites [2].

Polyethylene (PE) is a thermoplastic polymer consisting of long chains of the monomer ethylene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. With regard to sold volumes, the most important polyethylene grades are high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) [3].

Zirconium dioxide (ZrO_2), or more commonly known as zirconia, is non-flammable and has a melting point of about 2720 °C. The chemical and thermal stability of ZrO_2 allows its application as a good diffusion barrier.

Nanocrystalline zirconia was shown to have good electrical and mechanical properties with toughness values between 16 and 17 MPa.m^{1/2}. Hence, combining zirconia and polyethylene could make a stronger polymer with many potential applications. Conventional static tests, including tensile, bending, and impact tests, are usually performed to characterize the mechanical properties of composites [4-9].

The aims of the present work were to produce nanocrystalline ZrO_2 – filled PE composite sheets to investigate the influence of nanozirconia weight percentage on the tensile properties of high density polyethylene.

In addition, scanning electron microscopy (SEM) was used to examine the interfacial adhesion between the nanozirconia inclusions and the polyethylene matrix, as well as the nanozirconia particle distribution in the matrix.

EXPERIMENTAL WORK

Materials

The present work involved the use of as – received Relene M 60075 high density polyethylene (HDPE), produced by Reliance Industries Limited, India, with a density of 0.96 g/cm³ and a melting point of about 150°C, and nanocrystalline zirconia powder. The asreceived nanozirconia spherical particles powder was provided by MEL Chemicals, UK, and had a density of 5.83 g/cm³ and was only available in an overall average particle size of about 28 nm.

Experimental Procedure

Carefully weighed amounts of high density polyethylene and zirconia were mixed to produce samples with varying zirconia contents ranging from 0 % to 12 %, as is shown in Table (1). The weight of each mixed sample was about 100g. Both constituents, zirconia and polyethylene, were thoroughly mixed in a ball mill for about 24 hours and heated up in a mould to melt the polyethylene and make the sheets at a temperature of about 170°C. Heating rate was generally slow, initially at 5°C/minute and then was reduced to 3°C/minute as the melting point of polyethylene was approached. This was done in order to achieve homogeneous mixes and for the polyethylene to completely wet the zirconia particles.

Table 1: Chemical composition of zirconia–high density polyethylene composite samples

Sample number	HDPE weight (%)	Zirconia weight (%)
1	100	0
2	96	4
3	92	8
4	88	12

The composite samples were pressed into sheets; each sheet had dimensions of 200 mm length, 150 mm width and 2 mm thickness. Pressing was achieved using a Collin testing platen press type P300 P/M, at the laboratories of the Car Tires Manufacturing Complex, Tajora, Libya.

Pressing was carried out at a constant temperature of about 170°C and using a pressing time of 3 minutes. The sheets were left to cool down to room temperature in their moulds, which were then opened to extract the shaped sheets. The tensile specimens were cut out from the obtained pressed sheets.

Due to the readily availability of tensile testing, it was used to characterize the mechanical properties of these composite samples. Tensile testing was performed according to ASTM D 638M-89, on type M-I dog-bone specimens of 3.9 mm width and about 2 mm thickness, at the Polymers Research Centre laboratories, Tajora. The testing machine was an Instron 5566 with computer data acquisition system and load cell capacity of 908 kgf. Loading speed was 5.08 mm / min. The gauge length was 26 mm.

A JSM-5610 LV scanning electron microscope, at the Industrial Research Centre, Tajora, was used to study the morphology of the nanozirconia-polyethylene composite specimens and also to investigate the degree of dispersion of nanozirconia particles within the polyethylene matrix.

RESULTS AND DISCUSSION

A typical force-elongation curve for one of the prepared composite sheets is shown below, in Figure (1). The tensile properties which included maximum tensile strength and strain at maximum tensile strength were extracted from this figure.

Effect of Zirconia Addition on the Tensile Properties of ZrO₂ – PE Composite Sheets

Even though the maximum tensile strength at 12% ZrO₂ was higher than that for 8% ZrO₂, generally, the maximum tensile strength decreased with increasing percentages of zirconia in the composite sheets. As can be seen from Figure (2) shown below, there was a decrease in maximum tensile strength from a value of 14 MPa for un-modified PE to 10.7 MPa, when the zirconia weight percentage increased to 12%, see also Table (2) given below.



Figure1: A typical force-elongation curve for one of the composite sheets



Figure 2: Effect of zirconia weight (%) on maximum tensile strength

Table 2: Maximum tensile strength data for ZrO₂ -PE composite sheets

Sample number	Tensile strength (MPa) (± 0.5 MPa)
1	14.0
2	11.8
3	7.9
4	10.7

This decrease in tensile strength may possibly be due to the increased ease with which the polymer molecules can slip past each other. This reflects the increase in free – volume and the lowering of the interactions between the molecules which are caused by the presence of zirconia particles which allows more regions of the polymer structure to slide and hence giving a lower tensile strength.

Generally, the strain % at maximum tensile strength decreased with increasing percentages of zirconia particles in the composite sheets which is in agreement with the general trend reported in the literature. As can be seen from the figure given below, there was a decrease in strain to about 7.1 % when the zirconia content increased to 12 %.

However, the value of strain was about 8.5 % for pure polyethylene which rose to a value of 9.45% when the zirconia % was 4% (see Figure 3). Following this initial rise, the general trend was a continued drop in the value of strain % with increasing percentages of nanozirconia particles.

This decrease in strain would possibly be attributable to the polymer chains-zirconia particles joining together and this decreased the chains mobility and the % elongation for the polymer. As a result, the plasticity of the polymer decreased.

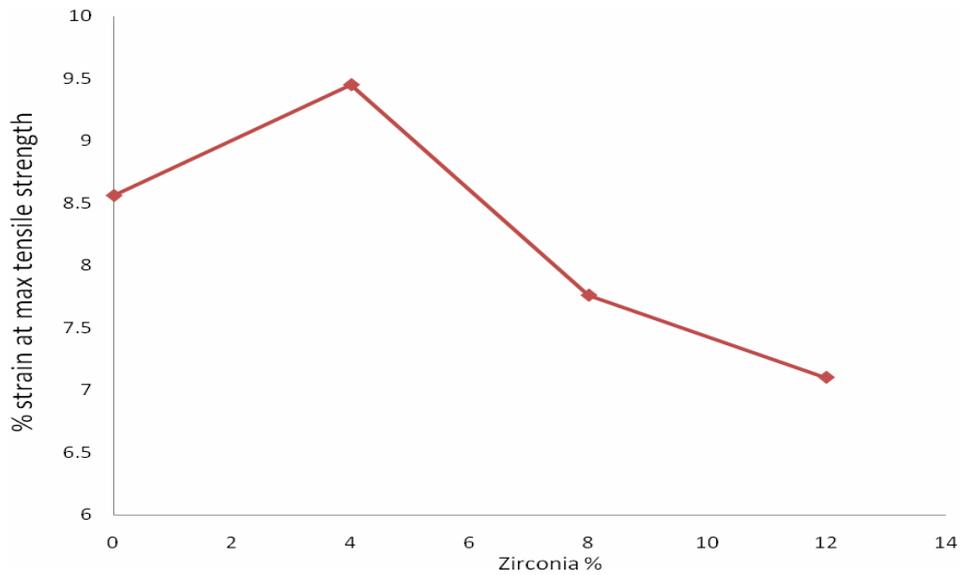


Figure 3: Effect of zirconia weight (%) on strain at max tensile strength

SEM

SEM investigation showed that the nanozirconia particles to be dispersed within the polyethylene matrix to a fairly good extent for the composite specimen containing 12% nanozirconia (see Figure 4).

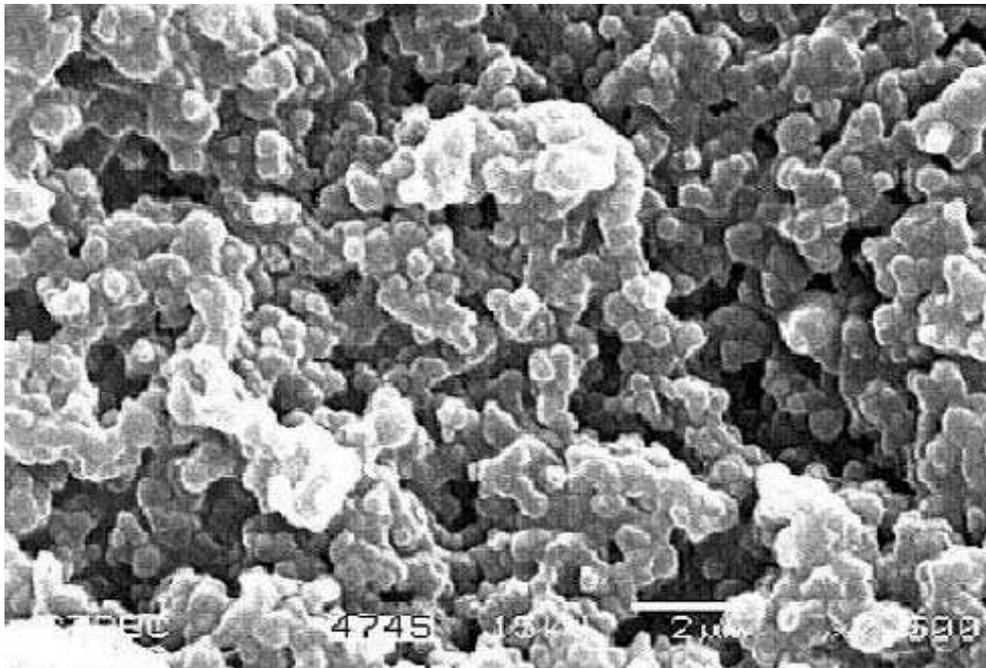


Figure 4: SEM micrograph of the composite sheet 12wt % nano zirconia – PE.

However, it seems from the obtained images that the interfacial adhesion between the zirconia inclusions and the polymer matrix is fairly poor due to the lack of a coupling agent.

CONCLUSIONS

Based on the results obtained in this study, the following conclusions can be drawn:

- The maximum tensile strength and the strain % at maximum tensile strength both decreased with increasing nanozirconia powder weight % in the prepared composite sheets.
- SEM micrographs seem to show that the zirconia particles to be fairly well dispersed within the HDPE matrix. However, the degree of interfacial adhesion appears to be low as the zirconia particles appear to be well – defined and separated from the HDPE matrix.
- In order to reach truly conclusive results on the influence of nanozirconia particles on the tensile properties of high density polyethylene it appears necessary both to improve the mixing procedure and to use a coupling agent.

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