PREPARATION OF ALUMINA – FILLED POLYETHYLENE COMPOSITES, TENSILE STRENGTH AND DYNAMIC MECHANICAL ANALYSIS TESTING

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الملخص

إن إضافة المواد المالئة غير العضوية إلى البوليمرات أثناء مراحل تصنيعها هو إجراء شائع ومتبع لما له من أثر في تخفيض تكلفة الانتاج وتحسين بعض خواص البوليمرات لهذا تم خلط مسحوق أكسيد الألومنيوم (الألومينا) بحجم حبيبي أقل من 38 ميكرومتر وبنسب وزنية تتراوح بين 0 % إلى 12 % مع بولى ايثيلين عالى الكثافة.بعد ذلك أجريت عملية كبس لهذه الخلطات المركبة من الألومينا والبولي ايثيلين عند درجة حرارة 170 درجة مئوية ولزمن قدره 3 دقائق لغرض الحصول على صفائح من مادة مركبة.تضمن هذا البحث تعريض صفائح المادة المركبة المنتجة لاختبار شد و تحليل ميكانيكى ديناميكى (Dynamic Mechanical Analysis, DMA) في مدى من درجات الحرارة تتراوح بين - 150 إلى + 150 درجة مئوية.

أظهرت النتائج المتحصل عليها انخفاض في مقاومة الشد القصوى مع زيادة محتوى الألومينا في المادة المركبة.بينما نتائج التحليل DMA بيّنت زيادة في معامل المرونة عند درجة حرارة الغرفة عند اضافة الألومينا بنسبة وزنية قدرها 3 %. ولكن لوحظ انخفاض في قيمة معامل المرونة لجميع العينات مع ارتفاع درجة الحرارة. كما تم استخدام التحليل DMA لقياس درجة حرارة التحول الزجاجي (Tg) حيث وجد أنها تقل مع زيادة محتوى الألومينا وهذا يدل على أن الالومينا أصبحت تعمل كمادة ملدنة (plastizer) حيث إن إضافتها أدت إلى انخفاض Tg من خلال تأثيرها على الحجم الحر (free volume) وكذلك قوة الترابط بين جزيئات البوليمر كما أن زيادة الحجم الحر وإضعاف قوة الترابط تؤدى إلى انخفاض Tg.

ABSTRACT

Addition of inorganic fillers to polymeric materials during processing is a common practice as it typically reduces the cost and improves certain properties of the material. Hence, alumina powder of particle size less than 38 µm was blended with high density polyethylene (HDPE) and then hot pressed at 170 ºC for 3 minutes to produce composite sheets. The weight percentage of alumina in the composite was varied from 0 to 12 %. The composite sheets were subjected to tensile testing and dynamic mechanical analysis in a temperature range of – 150 º up to +150 ºC.

The results showed that the maximum tensile strength decreased with an increase in the alumina content. The dynamic mechanical analysis (DMA) results showed the elastic storage modulus increasing slightly at room temperature with the inclusion of 3 % alumina, however, the modulus value decreased with increasing temperature for all the composite sheets. The glass transition temperature, T_g, was measured using (DMA) for pure polyethylene and the prepared composite sheets. T_g was found to decrease with increasing alumina content which means that the alumina

can be considered as a plastizer (T_g reducing agent). This reduction in Tg can be due to free volume increase and lowering of the interaction between the polymer molecules.

KEYWORDS: Alumina; Polyethylene; Composites; Dynamic Mechanical Analysis; Free volume; glass transition temperature.

INTRODUCTION

The toughness of composite materials filled with rigid inorganic particles will be improved or enhanced to different extents under given conditions, in addition to increased rigidity and strength [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].

Two very different types of ethylene polymers can be made: low-density polyethylene, which is made at very high pressures using a free–radical initiator, and high–density polyethylene, which is made using various metal–complex catalysts. The low–density polyethylene (LDPE) contains many short branches, mostly two to four carbons long and a few long branches of undetermined length, but long enough to have elasticity. High–density polyethylene (HDPE) theoretically has no branches [3].
Alumina (Al_2O_3) is non–flammable and has a melting point of 2050 ºC. The chemical and thermal stability of Al_2O_3 allows its application as a good diffusion barrier and from a toxicological view point, Al_2O_3 is non–toxic.

Polyethylene and Al_2O_3 are biocompatible. Combining these two materials could make a stronger polymer with many potential applications. For example, along with the typical arthroplasty applications for polyethylene, successful biocompatibility has recently been observed for an Al_2O_3 / polyethylene blood pump [4].

Conventional static tests, including tensile, bending, and impact tests, are usually performed to characterise the mechanical properties of composites. Because composite materials can undergo various types of dynamic stressing during service, studies on the dynamic mechanical properties of these materials are of great importance. Furthermore, because of the highly temperature–dependent mechanical properties of such composites, the application of a method that monitors property changes over a range of temperatures is critical. Similar to other properties, dynamic mechanical properties depend on types of filler, filler loading, filler dispersion, and filler–matrix adhesion [5]. Dynamic mechanical analysis (DMA), or dynamic mechanical thermal analysis (DMTA), is a sensitive technique that characterises the mechanical responses of materials by monitoring property changes with respect to temperature and/or frequency of oscillation. The technique separates the dynamic response of materials into two distinct parts: an elastic part ($E^{'}$) and a viscous or damping component ($E^{''}$). The elastic process describes the energy stored in the system, whereas the viscous component describes the energy dissipated during the process.

The ratio $E^{''}$ / $E^{'}$ is viscous response expressed relative to elastic response. This ratio reduces to sin δ / cos δ which is tan δ. Thus, the name "loss tangent" is appropriate. Dynamic mechanical measurements are very useful for analysing the correlation between structure and properties of polymeric materials [6].

The aims of the present work were to produce Al_2O_3–filled PE composite sheets to investigate the influence of Alumina weight percentage on the tensile properties of high density polyethylene. A further objective was to study the influence of alumina powder content on the dynamic mechanical properties of the prepared Al_2O_3–filled PE composite specimens.

EXPERIMENTAL WORK

Materials

The present work involved the use of as–received high density polyethylene (HDPE), with a density of 0.96 g/cm^3 and a melting point of about 150 °C, and alumina granules. The alumina, which had a density of 3.97 g/cm^3, was ball–milled and then the resultant powder was sieved to produce spherical particles with sizes less than 38 µm. This particle size range was expected to give better packing inside the voids of the polymer structure.

Alumina and polyethylene premixing

Carefully weighed amounts of high density polyethylene and alumina were mixed to produce samples with varying alumina contents ranging from 0 % to 12 %, as is shown in Table (1). The weight of each mixed sample was about 100g. Constituents, alumina and polyethylene, were thoroughly mixed and heated up to a temperature of about 170 ºC. This was done in order to achieve homogeneous mixes and for the polyethylene to completely wet the alumina particles.

Table 1: Chemical composition of alumina - high density polyethylene composite samples

Sample number	HDPE weight (%)	Alumina weight (%)
1	100	0
2	97	3
3	94	6
4	91	9
5	88	12

Alumina – HDPE composite sheets preparation

The composite samples were pressed into sheets; each sheet had dimensions of 200 mm length, 150 mm width and 2 mm thickness.

Pressing was carried out at a constant temperature of 170 ºC and using a pressing time of 3 minutes. The alumina particle sizes used were less than 38 µm and the alumina content varied from 0 to 12 gm.

Tensile testing

This was performed according to ASTM 638M-89, on type M–I dog–bone specimens of 3.9 mm width and about 2 mm thickness. 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.

Dynamic mechanical analysis

The instrument used in the present work was NETZSCH DMA 242. Measurements were carried out at a frequency of 1 Hz and amplitude of 200 µm and using a 3 point–bending fixture with a span length of 40 mm. Samples dimensions

(length x width x thickness) , in mm, were 40 x 12 x 3. Runs were made over a temperature range of - 150 to +150 ºC with a heating rate of 3 ºC / minute.
Figure (1) shows a picture of the DMA instrument which was used in the present study.

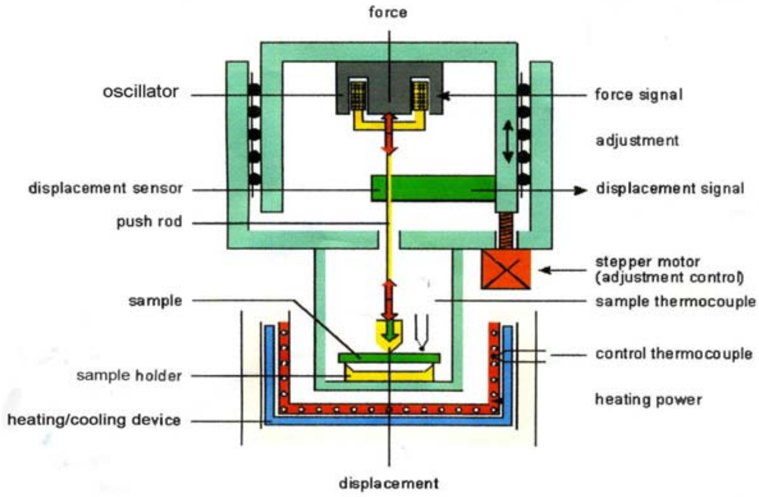

Figure 1: A diagram of the DMA instrument uesd in this work [after ref. 7]

The sample is supported on two edges and the end of the push rod applies load from the top. The distance between the two edges is in accordance with DIN53457. This method of deformation is ideal for materails with a high modulus such as filled or reinforced thermoplastics as the composite sheets produced in this work.

RESULTS AND DISCUSSION

Effect of Alumina Addition on the Maximum tensile strength of Al_2O_3–PE Composite Sheets

Generally, the maximum tensile strength decreased with increasing percentages of alumina 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 14.9 MPa for un–modified PE to 9.67 MPa, when the alumina weight ratio increased to 12 %.

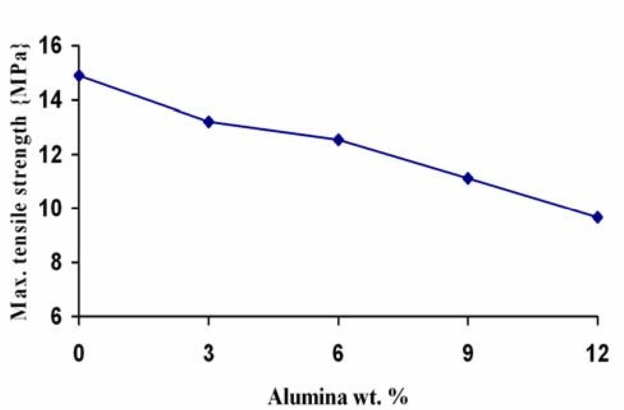

Figure 2: Effect of alumina weight % on maximum tensile strength.

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 alumina particles which allows more regions of the polymer structure to slide and hence giving a lower tensile strength.

DMA results

The dynamic mechanical properties of alumina – filled composites from – 150 ºC to +150 ºC were studied using DMA. Figures (3, 4 and 5) show the variation of the storage modulus ($E^{'}$), loss modulus ($E^{''}$), and loss tangent (tan δ) as a function of the temperature for pure polyethylene, 3 wt.% Al_2O_3 , and 6 wt.% Al_2O_3 , respectively.

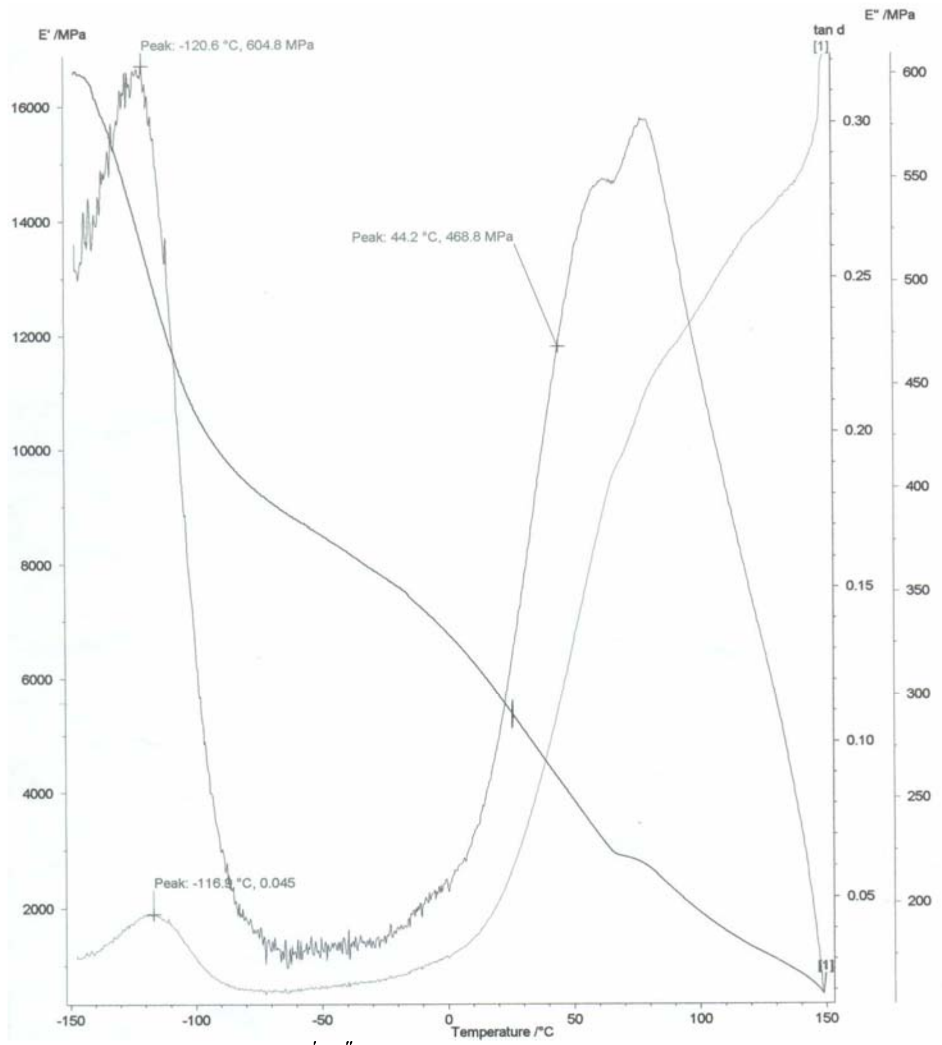

Figure 3: Variation of $E^{'}$, $E^{''}$, and tanδ with temperature for pure polyethylene.

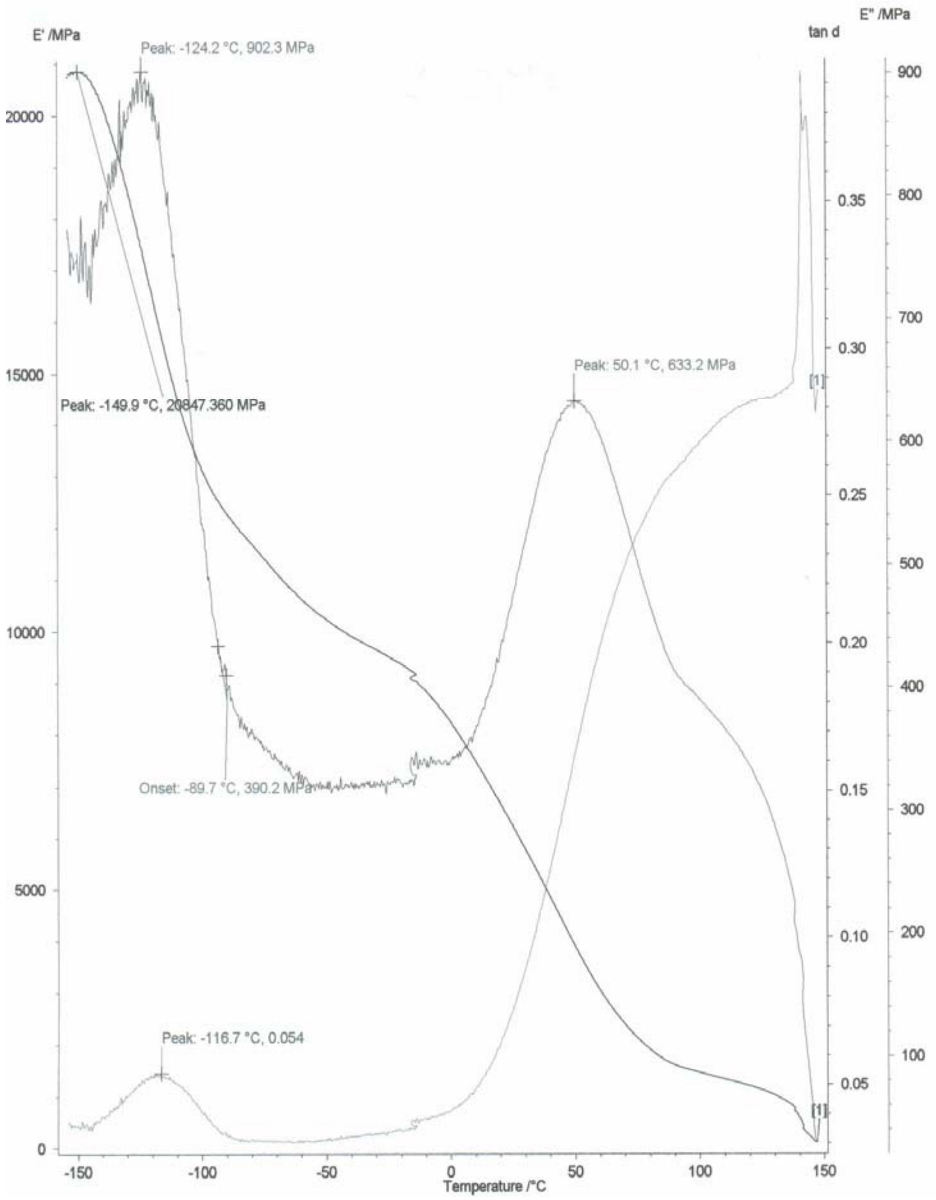

Figure 4: Variation of E′, E″, and tanδ with temperature for 3 wt% alumina – PE.

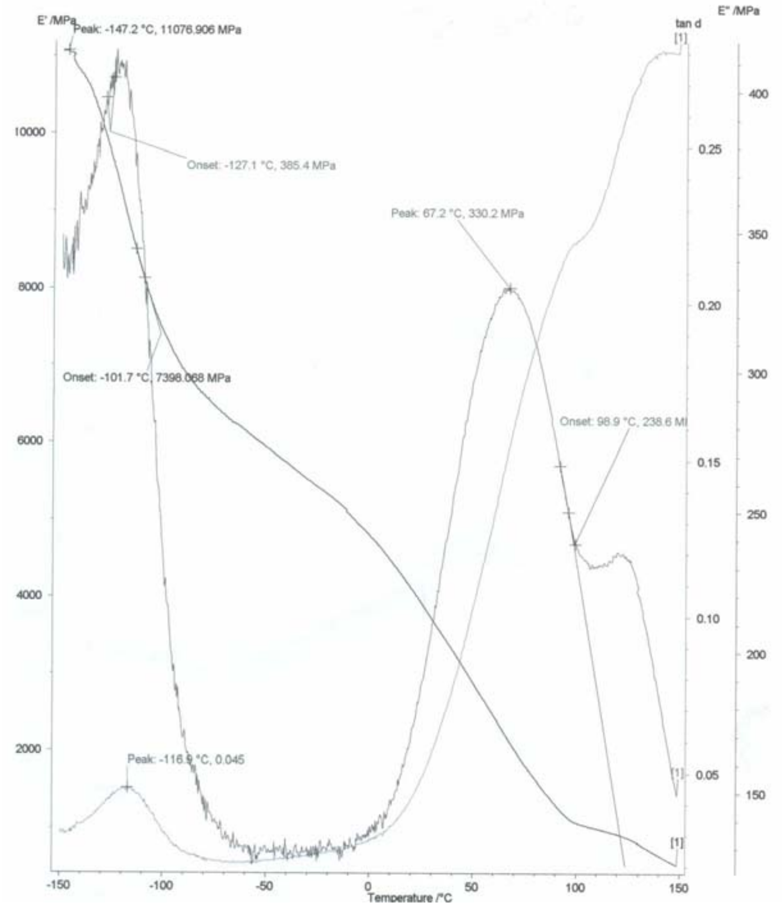

Figure 5: Variation of E$'$, E$''$, and tanδ with temperature for 6 wt% alumina – PE.

The storage modulus increased slightly as the content of alumina increased to 3 % at room temperature and decreased as the temperature increased. The storage modulus increase at room temperature would be expected with adding alumina because of the greater stiffness of the alumina and because the alumina generates a stiffer interface in the polyethylene matrix. For pure polyethylene, the value was about 5500 MPa at room temperature and decreased to 2000 MPa at a temperature of 100 ºC, whereas for the composite 3 % alumina–PE, the value of E$'$ decreased from about 7000 MPa at room temperature to a value of about 1500 MPa at 100 ºC. This may be explained by the increase in free–volume as temperature rises. The increase in temperature would obviously give energy to the polyethylene molecules which increases their ability to move past each other and hence leading to a reduction in the modulus E$'$.

The glass transition temperature, T_g, is characterised by a knee in the E$'$ curves and the maximum point in the E$''$ and tan δ curves. The temperature of the E$''$ peak often lies below that of the tan δ peak, and some workers prefer to report this lower value as T_g. The lower value is in better agreement with T_g values obtained from differential scanning calorimetry (DSC), which is a widely used method for T_g determination [8]. The obtained E'' curves show a reduction in T_g values as filler contents increase. For pure polyethylene T_g was – 120 ºC, and with an alumina content of 3 wt. % the value reduced to – 124 ºC, and with increasing the alumina content to 6 wt. %, the T_g value decreased further to – 127 ºC. This behaviour may be due to an increase in free volume due to the presence of alumina particles. The composites will acquire some increase in free volume when fillers are filled into the matrix materials. Free volume is the space a molecule has for internal movement and which increases upon heating. If the filler content is increased continually, the packing density is lowered which allows a higher degree of polymer molecular mobility. Hence a reduction in T_g value is observed as filler content is increased.

CONCLUSIONS

Based on the results of the present research, the following conclusions may be drawn:

- The maximum tensile strength decreased with increasing alumina weight percentage in composite sheets.
- DMA results showed that the elastic storage modulus, E', increased at room temperature with the inclusion of 3 wt % alumina into the polyethylene matrix. However, the value of E' decreased as temperature increased for all the prepared composite sheets.
- DMA measurements of pure PE and the alumina – filled PE sheets also indicated a reduction in T_g value as the alumina filler content increased.

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