ISSN 1991- 8690 الترقيم الدولي ٨٦٩٠ - ١٩٩١
website: http://jsci.utq.edu.iq Email: utjsci@utq.edu.iq

Effect of Alkali Lignin on Heat of Fusion, Crystallinity and melting points of Low density polyethylene(LDPE), Meduim density polyethylene(MDPE) and High density polyethylene(HDPE)

Moayad N. Khalaf

Chemistry Dept.- College of Science - Basrah University -Basrah Iraq

Abstract:

Use of alkali lignin as a filler for polymers had been many advantage: non corrosive, low cost because (it source from black liquor which is waste from cooking of pulp) and used to improve the physical and mechanical properties of polymers. Alkali lignin added to three type of polyethylene (LDPE, MDPE and HDPE) in several concentrations (10-50% wt/wt).Thermal study by Differential Scanning Calorimetry (DSC) for this composites was studied ,its found that the heat of fusion ΔH_f and crystallinity decreased until 30% in composites of MDPE and HDPE then raised in 40% and decreased in 50% while It's increased for LDPE composites until 20% then decreased in 50%. The melting points for HDPE composites with lignin were higher than MDPE and LDPE composites.

Introduction:

Composites made out of polymers were thought to be good thermal energy storage materials, in which the heat is stored as latent heat of fusion in the polymers. Thermal energy storage is a very important topic in present times. Heat is often available only at special times, for example solar energy during the day or heat from the combustion of wood. The latent heat storage is the amount of energy which is stored in a material when it changes its molecular structure, its phase or its state of hydration. The phase change could be the change between the solid and liquid phase as well as between the liquid and gaseous phase. But it could also be a change in the solid structure like a change between a crystalline and amorphous structure or between the amount of water absorbed in a material [(1)].There are several reports about thermal studies of composites polymers. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WXRD) were used to determine the degree of crystallinity and crystalline structure of low-density polyethylene (LDPE) reinforcement with TiO_2 nanopartical which enhanced mechanical, thermal, electrical, optical and barrier properties [(2)].

Low density polyethylene, a commercial paraffin wax with a melting point of about 57°C, a copolymer called ethylene vinyl-acetate and an exfoliated graphite powder were produced and investigated .The most important thermal properties of these compounds, like the heat conductivity, the heat capacity and the latent heat of fusion were studied. In a thermal cycling experiment and Differential Scanning Calorimetry analysis, it was found, that the copolymer as well as the graphite powder improve the stability of the material [(1)].

Lignin is an amorphous, aromatic biopolymer second in natural abundance only to cellulose and is obtained from almost all types of natural wood based resources. It is a byproduct of pulp and paper mills and is conventionally treated as a waste material having low economical usage [(3)]. Lignin use as filler to improved the physical and chemical properties and to decrease the cost of end product of polymers [(4)].

In the present study the thermal properties of polyethylene-alkli lignin composites in varying concentrations of lignin (10%-50%wt/wt) was studied by Differential Scanning Calorimetry (DSC).

Experimental:

Three grades of polyethylene were supplied by the state company for petrochemical industry in Basrah (LDPE 463, MI=0.3 g/10min., MDPE TR-401.MI=1.4g/10min. and HDPE M624, MI=6.0g/10min.). Alkali lignin (black liquor) supplied by the sate company for paper industry in Basrah. Water was removed from alkali lignin by rotary evaporator at 120^{o}C and used as it is. The alkali lignin was added in the percent (10-50% wt/wt). The polymer and alkali lignin was mixed by mixer-600 attached to Haake Rheocord meter at temperature=160^{o}C and RPM=64. DSC measurements of the composites was determinates by Du Pont thermoanalyser model 1090 with DSC unit(910) connected to microprocessor data station unit, was used in this study after being calibrated with standard materials.

Result and Discussion:-

The Crystallinity of polymer was very important property because it reflect the mechanical properties and it gives the idea of operation condition needs to fabricate the polymer. Also the measuring of the crystallinity and heat of fusion will gives some information about the ability of polymers such as thermal energy storage and energy transfer. The most important thermal properties of these compounds, like the heat conductivity, the heat capacity and the latent heat of fusion [6].The higher values of heat of fusion ΔH_f and crystallinity for 10% composites of MDPE and HDPE with lignin was 204J/g and 231J/g for ΔH_f and 71.8% and 81.4% for crystallinity , while for LDPE composite the higher value reached with 20% LDPE-alkali lignin composite with value 120 J/g for ΔH_f and 42% for crystallinity as shown in (fig.1)-(fig.6).This may attributed to the available free volume in the polymers, for that the LDPE with higher free volume will reach complete dissipation of the filler at 20% of the filler concentration .complete dispersion of the 10% of alkali lignin in polyethylene which lead to raise ΔH_f and crystallinity. As the percent of the alkali lignin increase and reach 30% in the composite the ΔH_f and crystallinity decreased, this effect can be explain by the free volume area between chains is small because of the high crystallinity for both polymers HDPE and MDPE (80% and 50% respectively) , the free volume is small to dissipate the lignin filler between the polymer chains , while in (Fig.1) for LDPE show increase in ΔH_f and crystallinity until 20% because LDPE have higher free volume between chains [7] (low crystallinity for LDPE 39%) compared with MDPE and HDPE which can dissipate higher quantity of lignin filler for that the interaction between lignin and polymer chains via the physical interaction was increases because lignin containing several polar groups such as hydroxyl, methoxy and carboxyl groups [8], this polar groups increase the intermolecular packing which increasing the crystallinity and heat of fusion of polyethylene composite, for the composite containing 30% percent lignin in the same figure show little decrease in ΔH_f and crystallinity then the value decreases until 50% due to the lignin polymer was amorphous with (T_g=112^{o}C)[9] for that the crystallinity and heat of fusion of the LDPE composite was decreased.

(Fig.2) , (Fig.3) show increase in ΔH_f in 40% lignin composites with MDPE and HDPE is 156J/g , 150J/g respectively and the same case in (Fig.5) , (Fig.6) for crystallinty is 55% and 52.8% respectively. The reason in this increase may be due to complete lignin filler dissipation and causes increase of the physical interactions with the increasing of the amount of lignin and increases the intermolecular packing then decreased in 50%.

Melting points for the composites are shown in (Table 1). The composites of HDPE give higher melting points than MDPE and LDPE composites. This effect depend on arrangement of polyethylene chains [10], HDPE have a high degree of arrangement chains means it have a much crystalline regions which need a high temperature to destroy the last crystalline composition while LDPE have a low degree of arrangement chains means little crystalline regions which need a low temperature

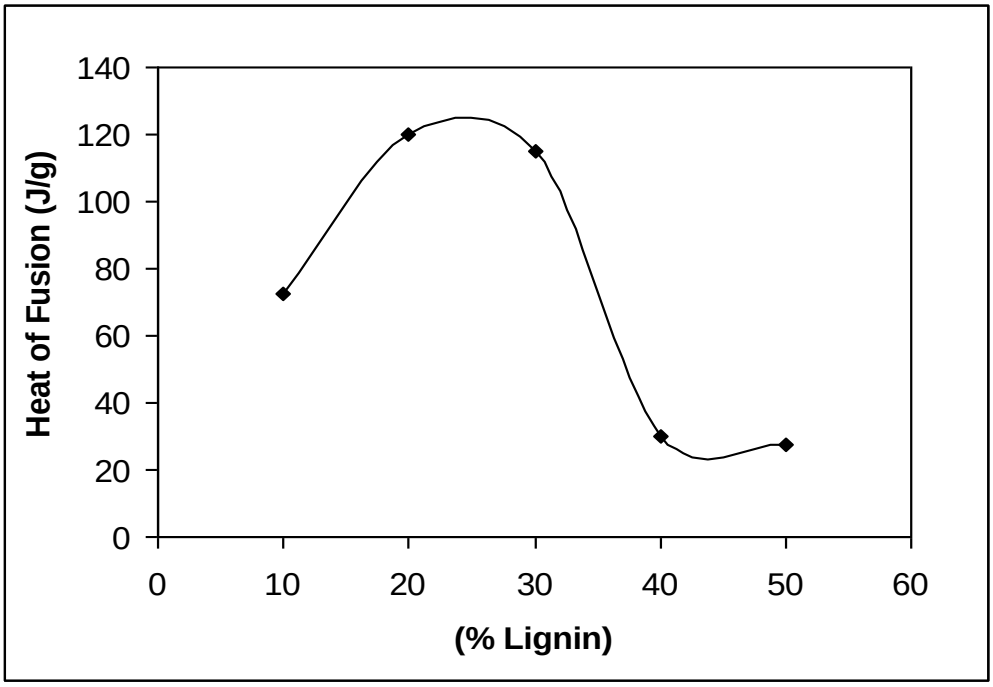

Fig.1 Effect of alkali Lignin concentration on the Heat of Fusion ΔH_f of LDPE.

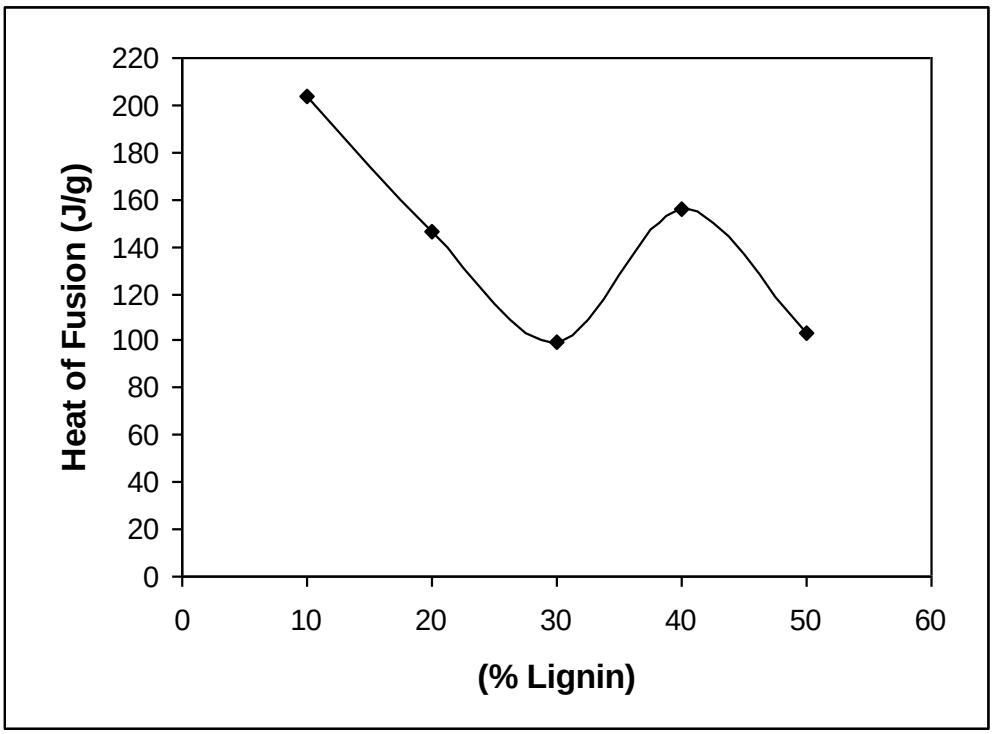

Fig.2 Effect of Lignin concentration on the Heat of Fusion ΔH_f of MDPE.

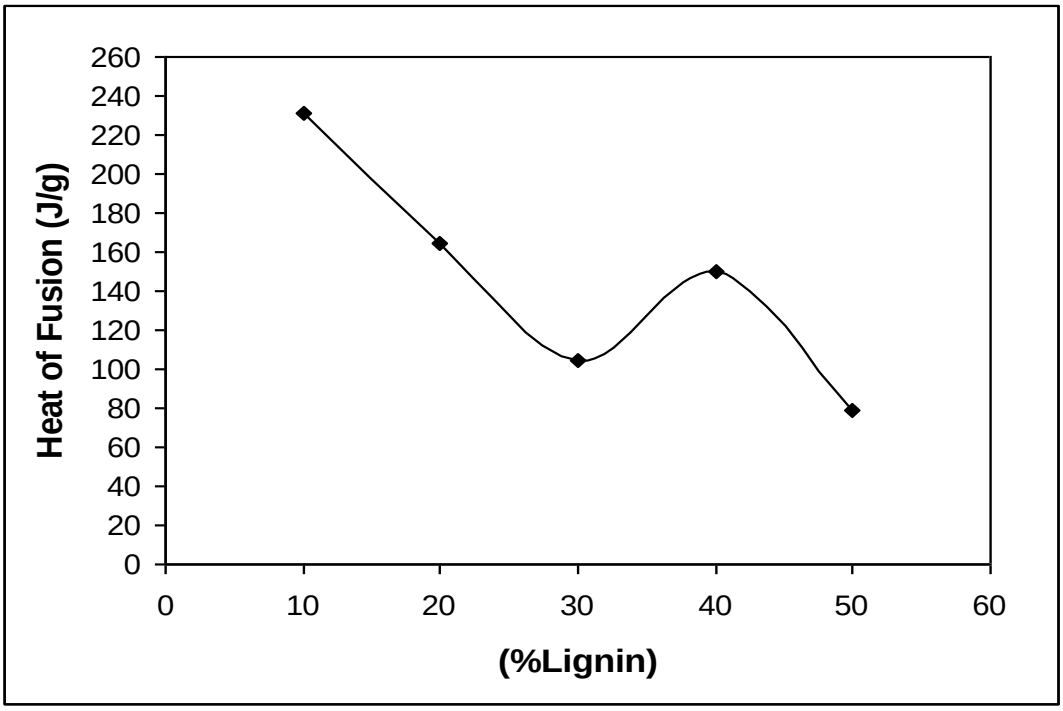

Fig.3 Effect of Lignin concentration on the Heat of Fusion ΔH_f of HDPE.

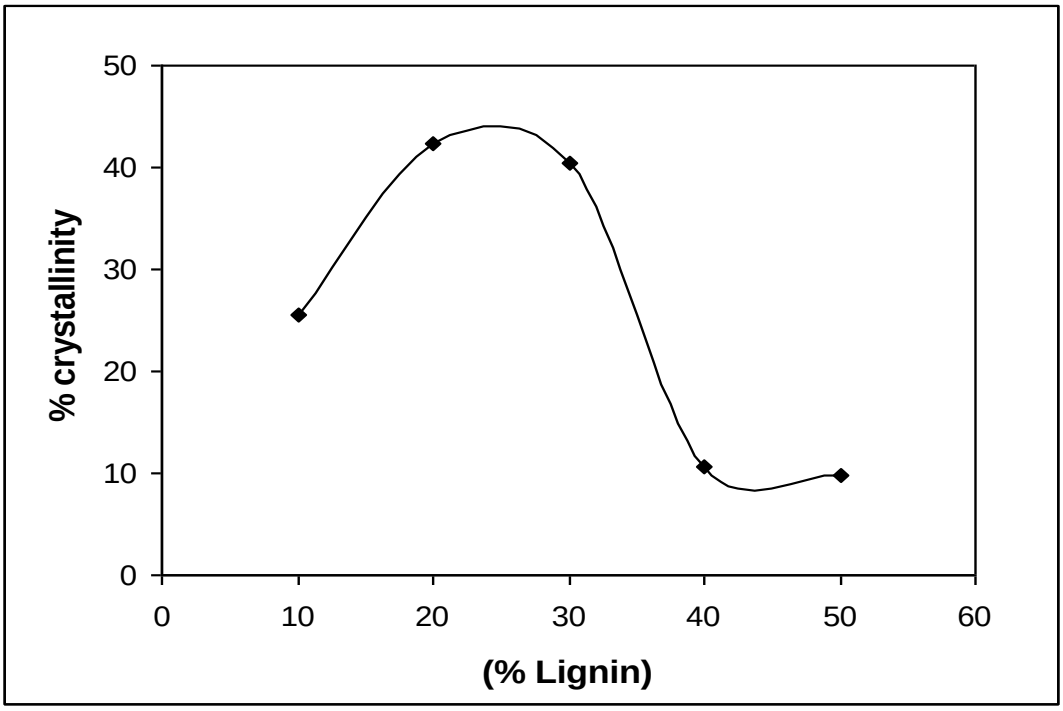

Fig.4 Effect of Lignin concentration on the Crystallinity of LDPE.

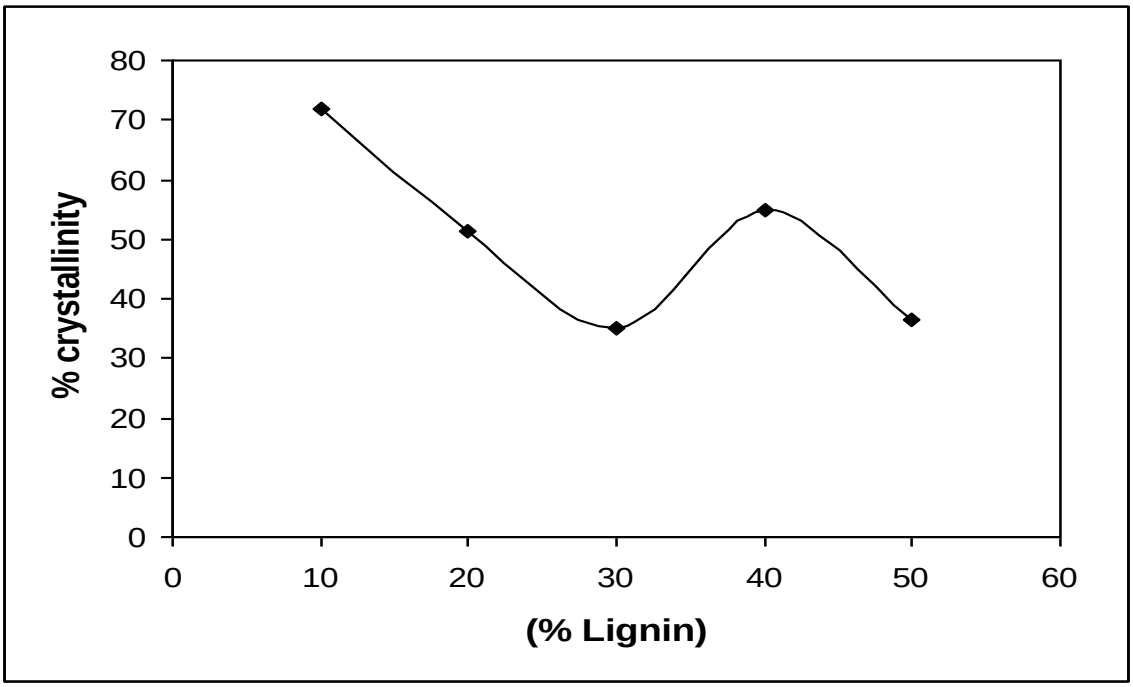

Fig.5 Effect of Lignin concentration on the Crystallinity of MDPE.

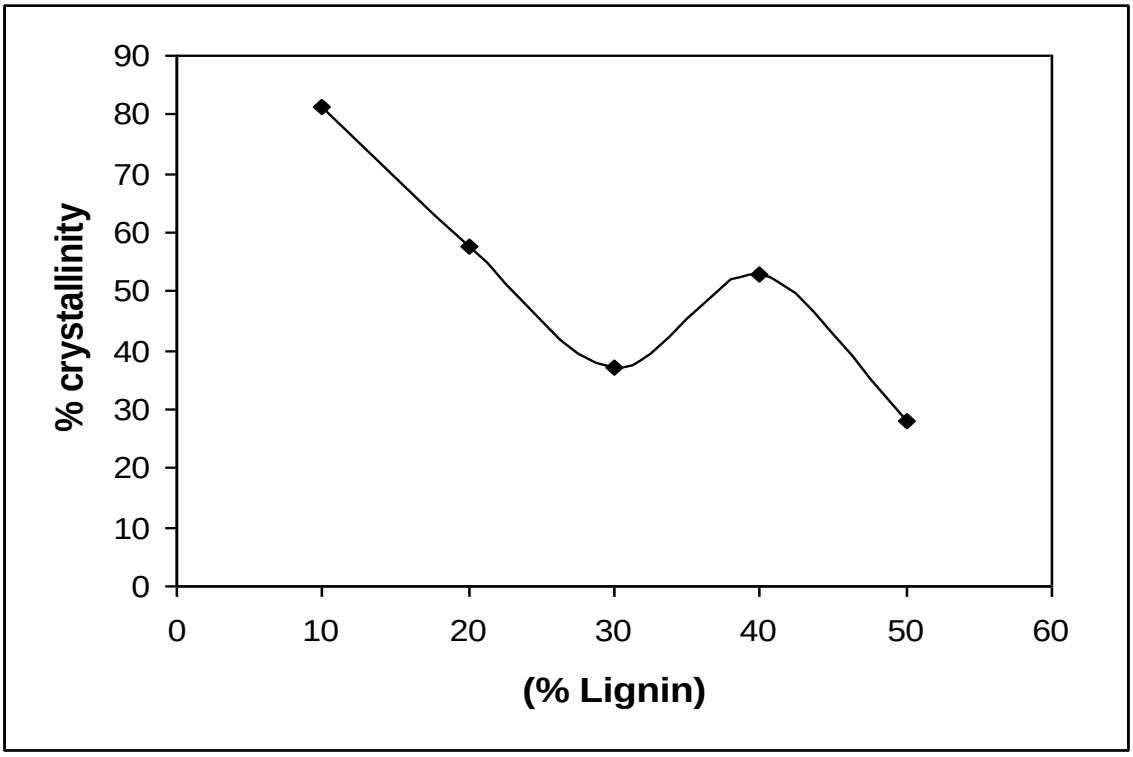

Fig.6 Effect of Lignin concentration on the Crystallinity of HDPE.

(Table 1) The melting point of Lignin composites with LDPE, MDPE and HDPE.

% Alkali Lignin	T_m (°C)		
	LDPE (463)	MDPE (TR-401)	HDPE (M624)
10	110.6	129.8	133.8
20	110.6	129.5	132.2
30	110.4	129.2	133.7
40	114.3	130.5	133.0
50	114.9	129.9	131.8

References

1- M. Bader , ph. D . thesis , The University of Auckland , New Zealand , (2002).

2- D. Ma , et al , Journal of Polymer Science: Part B: Polymer Physics , Vol. 43, (2005) 488.

3- W. G. Glasser and S. S. Kelley, "**Encyclopedia of Polymer Science and Engineering**", Vol. 8, Second Edition, john Wiley & Sons, (1987).

4- W.J. Frissd , " **Encyclopedia of polymer science and technology**" , Vol.6 , John wiley & sons , (1967) .

5- D. A.M. Hassan , M.Sc. thesis , Basrah University , Iraq , (2001).

6- T. Hatakeyama , "**Thermal Analysis Fundamentals and Applications to Polymer Science**" , Second Edition , John Wiley & sons , New York , (1999).

7- N. G. McCrum , C. B. Buckley and C. B. Bucknall , "**Principles of polymer engineering**" , Oxford university press , New York , (1997) .

8- K. V. Sarkanen and C. H. Ludwig , " **LINGINS - Occurrence -Formation - Structure and reactions** " John Wiley & sons , New York , (1971) .

9- T.G. Rials and W. G. Glasser , "Journal of Applied Polymer Science" ,Vol.37,(1989) 2399.

10- B. Wunderlich , "**Thermal Analysis of Polymeric Materials**" , Springer-Verlag Berlin Heidelberg , Netherlands , (2005).

الخلاصة

استعمال اللكنين القاعدي كمادة مالئة للبوليمرات فيها فوائد عدة منها :لايسبب التاكل ,ويقلل الكلفة كونه من فضـــلات عملية انتاج الورق (مصدره من السائل الاسود وهو ماده فضلات من عملية انتاج الورق) كما انه يعمل على تحســين الصفات الفيزياوية والميكانيكية للبوليمرات. تم أضافة اللكنين القاعدي الى ثلاثة اصناف من البولي أثيلين (البولي واطئ ألكثافة,البولي أثيلين متوسط الكثافة و البولي أثيلين عالي الكثافة) وبتراكيز تراوحت بــين(١٠ – ٥٠% وزنــا) . تــم دراسة المتراكبات الناتجة بأستخدام جهاز المسعر التفاضلي , وقد وجد أن طاقة الانصهار ودرجة البلوريــة تقــل لغايــة ٣٠% للمالئ في بوليمري البولي أثيلين متوسط الكثافة و البولي أثيلين عالي الكثافة ومن ثم تــزداد فــي النســبة ٤٠% وتنخفض عند النسبة ٥٠% أما بالنسبة للبولي أثيلين واطئ الكثافة فالقيمة ترتفع لغاية ٢٠% ثم تنخفض لغاية ٥٠%. في حين وجد أن درجة الأنصهار للبولي أثيلين عالي الكثافة الحاوي على اللكنين أعلى من ألبولي أثيلــين متوســط الكثافــة وواطئ الكثافة الحاويان على اللكنين أيضا .