

THERMAL DEGRADATION EFFECT ON THE FRACTURE TOUGHNESS OF GLASS FIBER REINFORCED UNSATURATED POLYESTER RESIN COMPOSITE

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Abstract

Samples of FRP prepared by applied unsaturated polyester resin as matrix reinforced by one layer woven glass fiber (0°/90°), using hand lay up method. The prepared samples are subjected to thermal aging at 85 ° C for different time in dryer oven up to 1200 hrs time and tested by unnotched sample impact tester to obtained the fracture toughness, polynomial relationships of order 5 found between G_c and Aging time decreasing G_c strongly to lower value. The Stress strain tests for aged to specific time and without aging samples by tensile test show that sample aged thermally tend to brittle behavior and lost its mechanical properties as aging time increase, while sample without aging show ductile behavior. FTIR analysis show decomposition of the polyester by creating new free radical and observed new peak wave number in transmission spectra due to fiber crystallization.

Keywords; thermal degradation, aging, composite, fracture toughness, polyester, impact

تأثير الآتلاف الحراري على متانة التكسير لمركب البوليمر الغير مشبع المقوى باللياف الزجاج

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الخلاصة

حضرت عينات من البوليمر المقوى باللياف باستخدام راتنج بوليمر البولي أستر الغير مشبع كقالب أم مقوى بطبقة واحدة من اليف الزجاج المتعامده (90° \ 0°) وبأستخدام تقنية التشكيل اليدوي. العينات المحضره عرضت للتعتيق الحراري بدرجة حرارة 85 م ولفترات زمنية مختلفه في فرن تجفيف ولزمن يصل الى 1200 ساعه كحد أقصى وفحصت العينات بجهاز فحص الصدم لعينات غير محززه لتحديد متانة الكسر حيث حصل منحني للعلاقه بين زمن التعتيق الحراري و G_c أقرب الى أن يكون ذو علاقته متعددة الحدود من الدرجة الخامس. حيث تنخفض قيمة G_c بشده الى القيمه الاقل. أن أختبارات الشد لاستحصال علاقته أجهاد - أنفعال لعينات غير معرضه للتعتيق وأخرى معتقه حراريا لمدد محدده ومختاره بينت أن العينات المعتقه حراريا تميل للسلوك القصيف وتفقد خواصها الميكانيكيه بزياده فترة التعتيق الحراري: بينما العينات التي لم تعرض للتعتيق الحراري أبدت سلوكا "مطيليا". أن تحاليل الطيف تحت الحمراء بينت تحللا للبولي أستر بتخليق جذور حرة وملاحظة أماكنية حصول تبلور للياف الزجاج من خلال ما ظهر من قمم جديده في العدد الموجي في طيف الامتصاص.

Introduction

One of the limiting factors in the application of plastics at high temperatures is their tendency to not only become softer but also to thermally degrade. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur (C. Su WOO & W. Doo KIM, 2006).

Thermal degradation of polymers is ‘molecular deterioration as a result of overheating’. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. It is part of a larger group of degradation mechanisms for polymers that can occur from a variety of causes such as: Heat (thermal degradation and thermal oxidative degradation when in the presence of oxygen), Light (photodegradation), Oxygen (oxidative degradation) and Weathering (generally UV degradation) (F. Nabil, 2003).

In general, the ability of a plastic to resist these degradation causes is called the ‘stability’ of the plastic and in this article we will concentrate on the process of thermal degradation with particular emphasis on thermal degradation in service as opposed to thermal degradation during processing (C 1303, 2000).

All polymers will experience some type of degradation during service and this will result in a steady decline in their properties. In fact, degradation is inevitable and the resulting chain reaction will accelerate unless the cycle is interrupted in some manner - the only real variable is how long it is going to take for thermal degradation to become evident and result in a loss in properties that is significant enough for the end-user to notice (M.Amin & M. Salman2006).

Theory

The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include: Reduced ductility and embrittlement , Chalking , Color changes , Cracking and General reduction in most other desirable physical properties(Wael I. *et al.* 2006). The dominant mechanism of degradation and the degree of resistance to degradation depends on the application and the polymer concerned(R. Cusson & Y. Xi,2003). The results are the same for most polymer families and significant property degradation can occur when thermal degradation does occur.

Polypropylene is very susceptible to thermal degradation, even at normal temperatures and must always be protected against thermal degradation(A. Porjazoska*et al.*2002). Thermal degradation causes chain scission and the reduced chain length reduces the molecular weight. This can considerably change the mechanical properties leading to highly reduced ductility and embrittlement and possible service failure.

Thermal degradation resulting chain branching and cross-linking reduces the melt flow and produces embrittlement and color changes(V. MACHOVÌ*et al.* 2008).

The Mechanism of Thermal Degradation

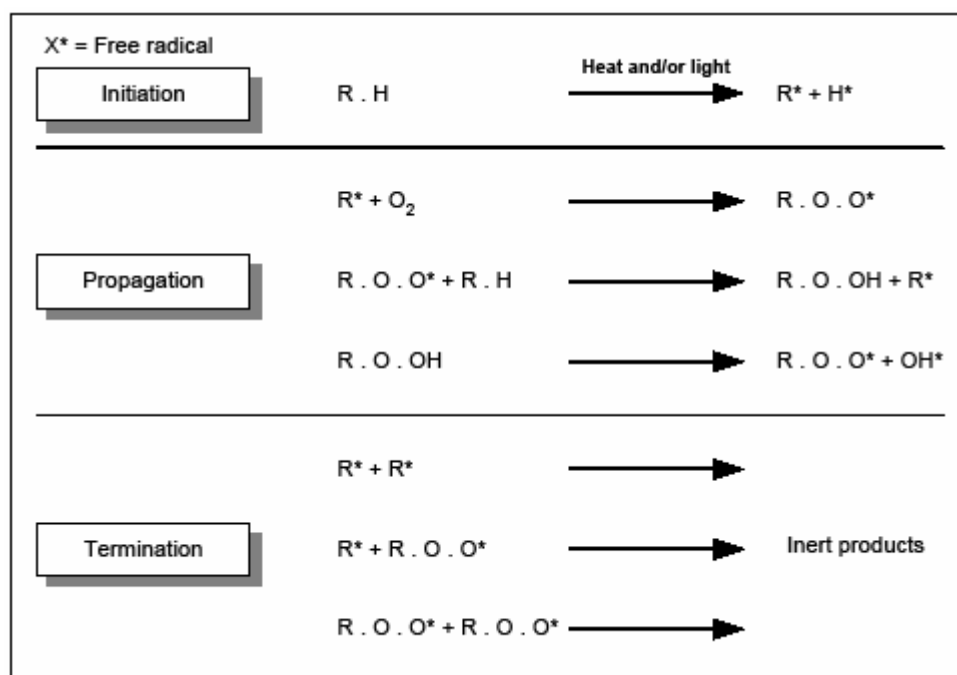
Most types of degradation follow a similar basic pattern (AV.J. JAROSLAVA, *et al.* 2009). The conventional model for thermal degradation is that of an autoxidation process which involves the major steps of initiation, propagation, branching, and termination.

The initiation of thermal degradation involves the loss of a hydrogen atom from the polymer chain (shown below as R.H) as a result of energy input from heat or light. This creates a highly reactive and unstable polymer 'free radical' (R^*) and a hydrogen atom with an unpaired electron (H^*). The strength of the C-F bond means that there it is much harder for thermal degradation to initiate.

The propagation of thermal degradation can involve a variety of reactions and one of these is where the free radical (R^*) reacts with an oxygen (O_2) molecule to form a peroxy radical (ROO^*) which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide ($ROOH$) and so regenerate the free radical (R^*). The hydroperoxide can then split into two new free radicals, (RO^*) + (*OH), which will continue to propagate the reaction to other polymer molecules. The process can therefore accelerate depending on how easy it is to remove the hydrogen from the polymer (C. Su WOO & W. Doo KIM, 2006).

The termination of thermal degradation is achieved by 'mopping up' the free radicals to create inert products. This can occur naturally by combining free radicals or it can be assisted by using stabilizers in the plastic.

A general mechanism for thermal degradation is shown below:



In some polymers it is also possible to get 'branching' of the polymer chains, this is where two polymer chains become linked together and results in cross-linking and embrittlement of the polymer. In some cases, thermal degradation shows no effect for some time and when it occurs the onset of significant thermal degradation can be very rapid, i.e. there is a gestation time before anything appears to happen and then the degradation is both rapid and catastrophic. This can occur particularly when the stabilizer is a sacrificial one - when it is completely exhausted then degradation can occur unchecked. In this case the mechanism is not a completely standard thermally controlled mechanism.

In other cases, the test temperature affects the operation of the stabilizer. Accelerated testing at high temperatures can then give misleading results if the stabilizer itself is not operating correctly or is operating in a different way to the way it would operate at normal service temperatures.

The linear elastic fracture mechanics (LEFM) defines the fracture toughness as the material resistance to the growth of the crack or flaw. Some texts relates this toughness to the strain energy release rate G_c given by (O. Ozcelik, *et al.*, 2009), :

$$G_c = dU_{el} / dA \quad (1)$$

Where U_{el} is the elastic strain energy stored within the loaded sample and A is the crack area. The response of the plastic material to an external load is not unique. they are either brittle or ductile; depending on test type and on test condition. To obtain more accurate impact data the system was then improved as an instrumented Pendulum impact tester (M. Ito 2009).

The aim of the present work is to study the effect of thermal degradation by thermal aging on the fracture toughness and other mechanical properties of glass reinforced unsaturated polyester polymer composites. Alternatively a remarkable thermal effect is observed for G_c values with the specimen aging time. Such inconsistency with direct G_c values are not suggests some reconsideration for the energy terms expressed as U_{el} .

Experimental

Materials and Sample preparation

The resin used as a matrix for the composite was Vipal H265 unsaturated polyester resin. Through the casting process the matrix was hardened by adding 0.5 gm of cobalt naphthenate to 100 gm polyester and accelerated by adding 2 gm of methyl ethyl ketone peroxide (MEKP) at a concentration of 0.02 w/w of the matrix. glass fiber of (110 gm/m^3) density woven (0/90) used as reinforced fibers with one layer for all samples with 20 % w/w fiber to composite ratio and (2 mm) thickness.

A measured quantity of unsaturated polyester resin mixed (MEKP) for rapid curing was poured on a pre-weighed amount of woven E- glass fibre which was placed in a mould. The mould was coated with a semi-permanent, polymer mould release agent, Frekote FRP90-NC. After pouring the resin, each layer was left for a few minutes to allow the resin to soak into the fibre mat. Trapped air was gently squeezed out using a roller. The glass fibre and polyester resin were then left for about 3 min to allow air bubbles to escape from the surface of the resin.

The panel was left to cure at a temperature of 22 °C for 24 h before being removed from the mould. Subsequently, post-curing was carried out at a temperature of 60 °C for 2 hr.

Sheet $20 \times 20 \text{ cm}^2$ area of glass fiber prepare to cast G/UP with one layer of fiber, making the composites using hand lay-up technique.

Aging process

To carry out thermal degradation at given temperature and time, the prepared samples are placed in an electrical oven at 85°C for different aging time ranged from 50 hrs aging in first step and by 50 hr. aging time interval increasing In each step ,up to 500 hrs. and from 500 to 1200 hrs. by 100 hrs. increasing aging time interval in next steps according to (ASTM D3045 - 92(2010))(ASTM D3045(2010)).

Cooled the samples in room temperature for 24 hrs. before impact test .

Tests

Impact test

Samples of (12)cm length,(18) mm width and (2)mm thickness unnotched tested by (XJU-22) Pendulum impact tester with (5) Joule energy meeting (ASTM D258-ISO180) , three tests for each aging time samples and one sample for each time and taking average value for each test. G_c value obtained using eq. (1) after measurement the crack area.

Tensile Test

A universal testing machine (Sanghai Mobis, China) is used to perform tensile tests for samples without aging and samples aged at 100,300,500 and 1200 hrs. The resultant data are processed via an attached computer and stored as an excel charts. These charts are ready to process and extract useful property results.

Optical Microscopy

In addition, an optical microscope (Bel, Italy) is used to observe the morphology of the failure zones. Micrographs of these zones are obtained with the aid of an attached camera to the microscope.

FTIR Test

In order to explain the impact and tensile test results; FTIR spectrographs are obtained for selected glass fiber resin reinforced unsaturated polyester composites samples (with and without aging) and sample of unsaturated polyester resin without reinforcement and without aging also. The FTIR spectra are measure using shimadzu (USA) instrument with resolution of 4[1/cm] and in the range 400-4000 cm^{-1} . However, for clear appearance of the shifts in the absorption bands; only the range of 400-1200 cm^{-1} is found useful and presented in this study.

Results and Dissuasion

The strain energy released to fracture materials obtained from impact test for each sample aged to define aging time used to measure the fracture toughness G_c with measured a crack area for each samples , these results for G_c drawing with aging time in fig. (1), this figure show highly decreasing of G_c with increasing aging time for interval rang approach about 500hrs ,slow decreasing of G_c after 500hrs time aging best fitting for this curve found to be polynomial fitting of order (5), that is indicated that aging caused thermal degradation which change the fracture toughness strongly after some time appear in figure from first aging before about 500 hrs, and slowly after this time but change strongly. Stress strain curves of sample without aging appear with ductile behavior(fig. 2) with highly mechanical properties elastic modulus ,tensile strength and yield stress ,highly plastic deformation region .curves of aging samples showed change in

mechanical properties and also fracture behavior, sample 100 hrs aged remain within ductile behavior with lower plastic deformation region compare with sample without aging.

Third curve in figure 2 showed the strongly change starting in fracture behavior, where this curve for sample aged to 300 hrs since no plastic deformation region found and the curve is brittle behavior, so in as curve 4 and 5 for samples aged to 500 hrs and 1200 hrs which fully brittle behavior and low mechanical properties. The transition from ductile behavior for nonage sample in fig.(2) to embrittle behavior or brittle behavior for aged sample in fig.(2) as get 'branching' of the polymer chains, this is where two polymer chains become linked together and results in cross-linking and embrittlement of the polymer (A. Katz *et al.* 1999).

T_g of unsaturated polyester resin about $(69)^\circ\text{C}$ as Known ⁽¹²⁾, so thermal degradation occur if materials subjected to over T_g temperature.

Decreasing in mechanical properties as time of aging increase as shown for Elastic modulus in fig.(3), Yield stress in fig.(4) and tensile strength in fig (5).

Fig. (6) FTIR spectra showed shifted for many peak as 742.59, 906.54, 939.33, 1068.56 and 1128.36 cm^{-1} in addition to new peaks result in the spectra of aged 1200 hrs sample as shown in fig.(6) as 418.55, 563.21, 669.3, 881.47 and 920.05 cm^{-1} due to two reason, the first; formation of free radical' (R^*) in the first step of thermal degradation mechanism formation, and the second think that as a result for glass fiber crystallization for highly aging time.

A unsaturated in plane deformation at 1070 cm^{-1} , unsaturated, aromatic out-of-plane bending deformations at 744 cm^{-1} and 705 cm^{-1} . In Up resins, there can be two or more different sources of aromatic moieties, usually from styrene and phthalic acid anhydride.

Most of characteristic of FTIR spectra of Up resins is strong carbonyl stretching between $1725\text{--}1730\text{ cm}^{-1}$ which out of the scope of this work, and two other band characteristic for oxygen containing groups at 1285 cm^{-1} and 1125 cm^{-1} (U. Knutviken & P. Kyllonen, 2006) explain why UP resins can become more brittle with age, especially if curing process is not carefully balanced by initiators, accelerators and inhibitors. The termination of thermal degradation is achieved by 'mopping up' the free radicals to create inert products. This can occur naturally by combining free radicals or it can be assisted by using stabilizers in the plastic ⁽⁶⁾.

In fig. (7) morphology image cracks and craze appear in the surface of highly aged samples as a result of thermal degradation.

In fig. (2) the stress strain curve of 1200 hrs after tensile stress reach its maximum value, did not drop to zero value directly, but in steps which each step of these represent one band of fiber cutting while in all other sample: the sample failure reached without fully cutting fiber but just matrix failure, at tensile sample 1200 hrs no fibers pull out for sample from matrix found. As a direct effect of thermal degradation by thermal aging white - yellow color of the normal specimen before thermal aging change to brown color after 200 hrs aging.

Conclusions

1- The thermal cycling of the tested samples shows an important effect on their final mechanical properties. The FRP should not be used at temperature above there glass transition temperature (T_g). It is recommended FRP composite have a T_g at least 30°C above the maximum usage temperature.

- 2- Thermal aging decrease fracture toughness of glass fiber reinforced unsaturated polyester resin composite as a polynomial relationship .
- 3- Thermal aging decrease yield stress , Elastic modulus and Tensile strength.

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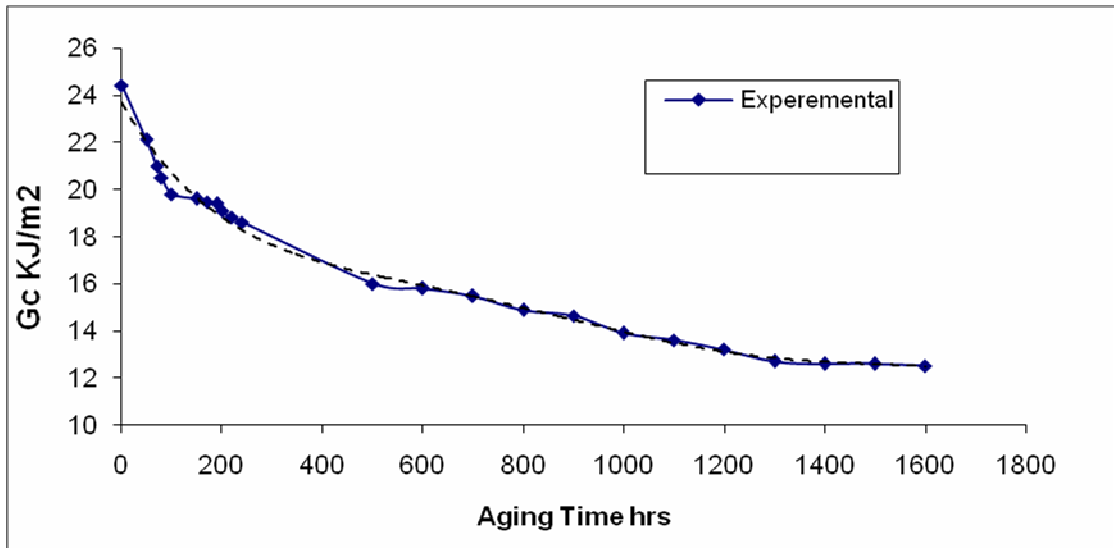


Figure (1) fracture toughness G_c –Aging time relation.

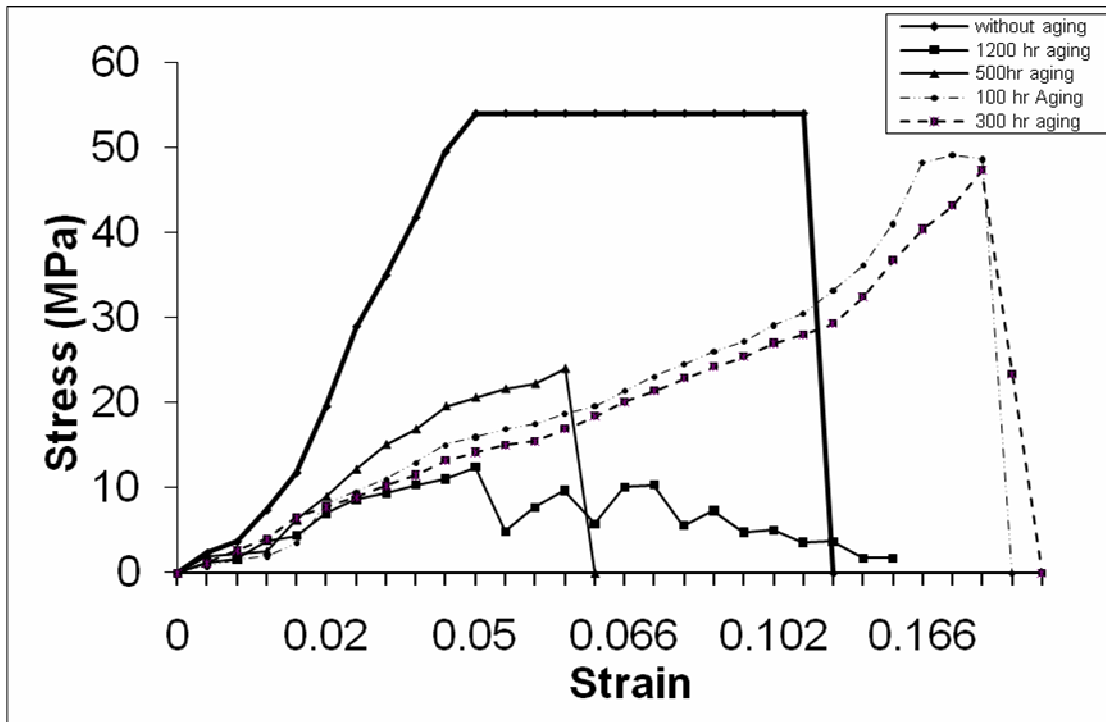
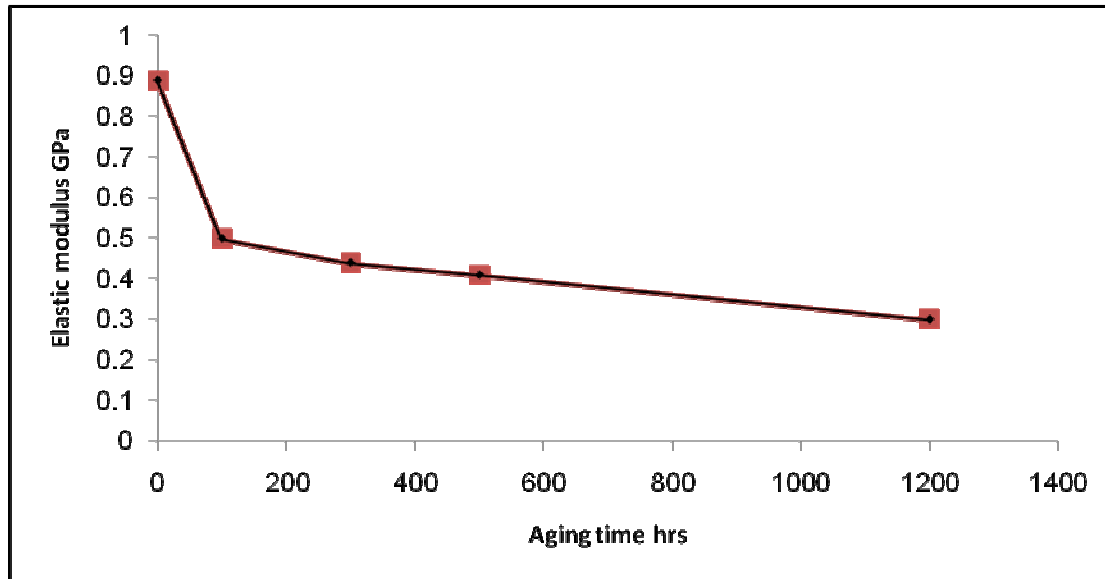
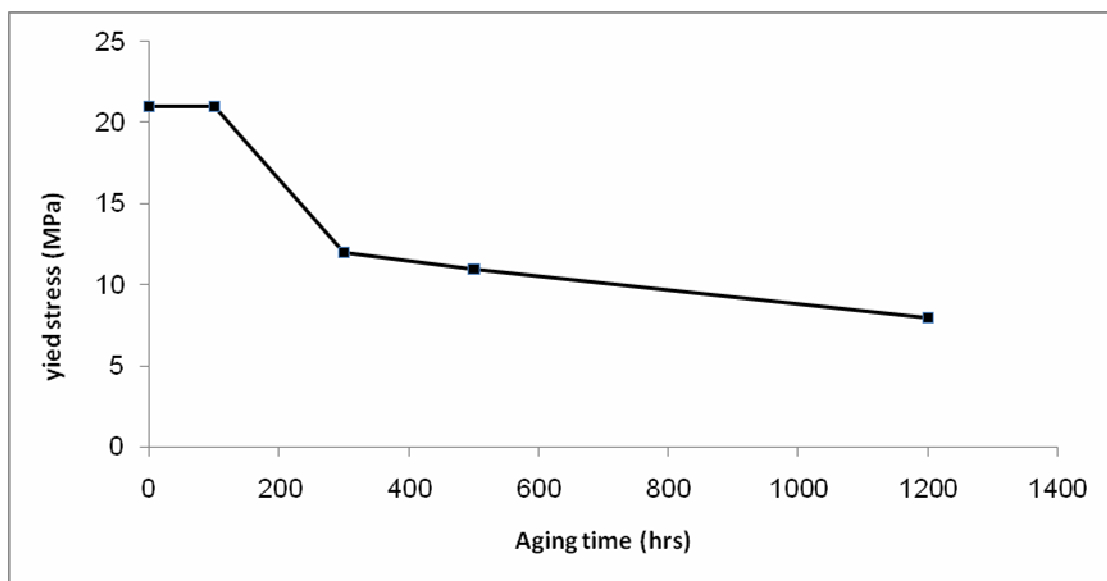


Figure (2) Stress –Strain curves for nonage sample and 100,300,500 and 1200 hrs aged samples.



Figure(3) Elastic Modulus – Aging time relation.



Figure(4) Yield stress –Aging time relation.

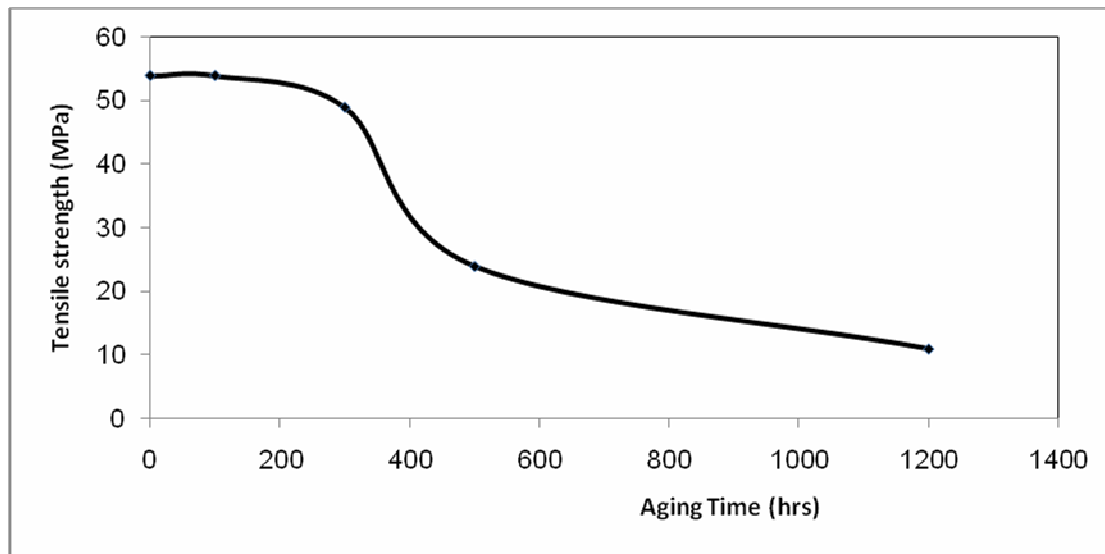


Figure (5) Tensile Strength – Aging time relation.

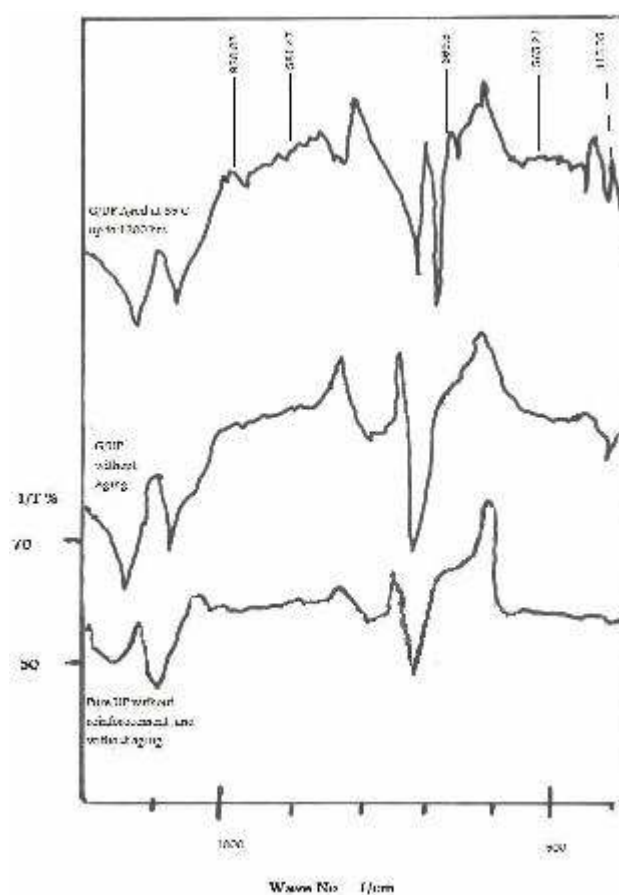


Figure (6) FTIR spectrum for nonage, 1200 hrs aged glass fiber reinforced unsaturated polyester resin and pure non aged unsaturated polyester .

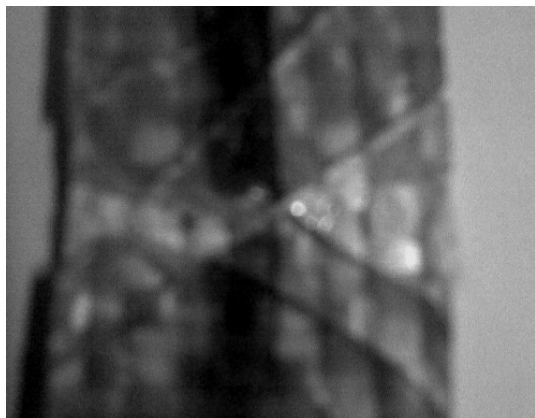


Figure (7) Morphology of cracks and crazes on aged sample surface.