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Relaxation processes and fatigue behavior of crosslinked UHMWPE fiber compacts

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Abstract

This paper presents a study of the fatigue behavior, mechanical properties and relaxation processes of UHMWPE fiber compacts as a function of structural parameters and crosslinking. UHMWPE compacts with optional crosslinking are produced by compressing the fibers under high temperature and pressure. The results of static flexural and tensile mechanical properties show that crosslinking improves the fiber–fiber coalescence and the stress transfer mechanism, which control the transverse and shear properties as well as the longitudinal properties in the fiber dominated direction. The dynamic mechanical testing identifies the typical relaxation peaks α, β and γ the main difference between the non-crosslinked and the crosslinked compacts being slightly higher storage modulus values and absence of significant β transition in the latter. The results imply that the formation of a crosslinked structure at the interface prevents transcrystallization. Finally, the fatigue results for loading at an angle to the fiber, for which damage is matrix and interface dependent, show that by crosslinking in the coalesced fiber skins, the resistance to cyclic loading and damage propagation is improved more than by the alternative of matrix crystallinity. The unique fatigue performance of the filament wound compacts is expressed by very low both absolute and scaled degradation rates.

Keywords: A. Polymer matrix composites; E. Filament winding; B. Mechanical properties; B. Thermomechanical properties; B. Fatigue

1. Introduction

Relaxation processes in polymers are of considerable interest for obtaining better understanding of the long-term stability of potential devices fabricated from these materials. Three second-order phase transitions are generally identified in polyethylene, which are notated in descending order from the melting temperature as α, β and γ [1,2]. These transitions are classified as either primary or secondary processes according to the significance of their effect on the mechanical properties of the polymer. In general [1], the γ relaxation at around −120 °C is identified with the glass transition, the β relaxation below 0 °C is related to motion of loose chain folds at the lamella surface, and the α relaxation in the temperature range of 50–120° C is associated with motion (rotation) of short molecular sequences in the crystalline region. In PE/PE composites, the presence of the fibers induces additional effects on the dynamic properties, as investigated by our group [3]. The presence of fibers and transcrystallization on their surfaces produce higher constraint levels, which in turn limit molecular mobility. As a result, the activation energies of all three relaxations are higher and a more prominent β relaxation occurs in transcrystalline PE/PE composites [3,4].

The fatigue behavior of composite materials is complimentary to the dynamic mechanical study of the relaxation processes for the purpose of understanding

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and improving the long-term engineering service conditions – noting that mechanical fatigue is the most common type of failure of composite structures in service [5]. The fatigue failure mode of composite materials is an explicit function of the angle between the fiber direction and the applied load; higher fatigue stresses are attributed to smaller angles [6]. The overall fatigue resistance is determined by the rate of degradation, which depends mostly on the properties of matrix and the fiber-matrix interface [7]. Accordingly, our study of the fatigue behavior of flat filament-wound PE/PE composites focused on the effects of winding angle, the fiber volume fraction and the degree of crystallinity of the matrix. An important finding was that the fatigue rate of degradation decreased with the degree of crystallinity [8,9].

A significant property-improving factor in polyethylene is crosslinking, generating better wear resistance, fatigue life, thermal stability and mechanical properties. Static mechanical testing of unidirectional composites shows that through crosslinking of the matrix, the mechanical properties of UHMWPE fiber-based composites improve by an order of 20% [10]. Even hot compacted UHMWPE fiber structures (developed originally by Ward [11]) possess improved mechanical properties due to crosslinking, attributed to stronger fiber–fiber bonding via the crosslinked network formed at their skins [12].

The relaxation processes and fatigue behavior in filament wound PE/PE composites [3,8,9] and the mechanical properties of crosslinked and non-crosslinked unidirectional and filament wound UHMWPE fiber compacts [10,12] were studied recently, emphasizing the conditions for property enhancement. The present study aims at investigating the UHMWPE fiber compacts, first by completing the study of the effect of reinforcing angle, and then by exploring the crosslinking effect on fatigue life (rate of degradation) and relaxation processes.

2. Experimental

2.1. Materials

Commercial UHMWPE fibers (Dyneema SK-75, DSM, The Netherlands) were used as reinforcement. The fibers have a nominal tensile strength of 3.8 GPa and modulus of 118 GPa. Dicumyl peroxide (DCP) (Lupersol 101, Atochem, Inc.) was used as crosslinking agent.

2.2. Sample preparation

Unidirectional UHMWPE fiber compacts were prepared by pulling the fiber tow through a bath of DCP solution and winding unidirectionally on a flat mandrel to the desired thickness, followed by drying in a fume-hood, to remove the hexane. DCP-treated preforms were laid out in a mold and pressed under 49 MPa at 145 °C for 30 min (Carver laboratory press, model 2518), followed by water-cooling under pressure, to obtain a unidirectional fiber compact. Non-crosslinked fiber compacts were obtained by using an untreated fiber tow.

Filament wound samples were obtained using a bench winder (Burlington Instruments Co., Vermont) as described in [8,9]. A flat mandrel (2.5 mm wide, 0.5 mm thick and 135 mm long) was used, onto which the fibers were wound at a constant angle relative to the mandrel axis (the winding angle, see Fig. 1). The number of layers was three. The resulting preform was carefully removed from the mandrel and heat-compacted at 145 °C under 31 MPa for 30 min, followed by ice-water cooling. The final winding angle was ±50°. The preparation process for DCP treated hot-compacted filament winding preforms was the same as for the untreated samples, except that the preforms were immersed in cold DCP/*n*-hexane (10% w/w) solution for 5 min, and dried in a fume hood in order to remove hexane.

2.3. Testing

Flexural mechanical testing was performed in three-point bending on a universal testing machine (Instron 4502) at a loading rate of 10 mm/min and loading span of 30 mm (span-to-depth ratio of 17). The interlaminar shear strength was measured at the same conditions under loading span of 14 mm (span-to-depth ratio of 7). Tensile mechanical testing was performed on the same universal testing machine-Instron 4502. The loading rate was 10 mm/min and the gage length was 15 mm. All the results were determined, based on the average value of five specimens.

Tensile dynamic mechanical tests were conducted by a dynamic mechanical thermal analyzer (DMTA, model MKII, by Polymer Laboratories Ltd, Loughborough, UK). All samples were tested at various frequencies (0.3, 1, 3, 10, 30 Hz), in a temperature range of −130 to 130 °C, at a heating rate of 0.5 °C/min, under a constant tensile load of 4 N for non-crosslinked and 8 N for crosslinked samples, in longitudinal loading and 0.4 N for both crosslinked and non-crosslinked samples in transverse loading. The peak-to-peak displacement was 32 μm. The gage length of the specimen was either 20 or 30 mm, the thickness approximately 0.3 or 0.8 mm and the width approximately 3 or 8 mm for longitudinal and transverse loading, respectively. Specimen clamping was followed exactly the recommended procedure in the *Operators' Manual* to ensure optimum clamping pressure. That procedure resulted in a torque of 40 cNm on the clamping screws.

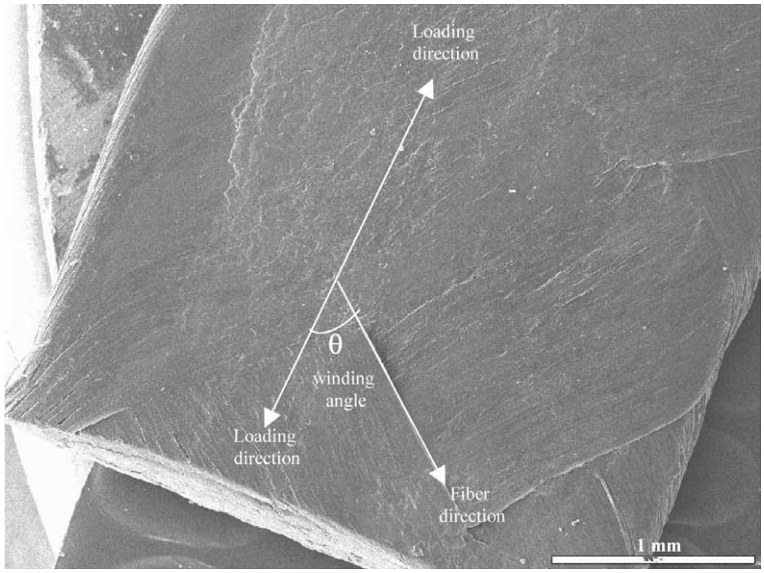

Fig. 1. A cross-section of a filament wound compact.

Fatigue tests were performed at room temperature under tension–tension sinusoidal stress control, using a closed loop servo hydraulic MTS 858 Mini Bionix testing machine. Load was imposed to ramp to the maximum value at a loading rate of 8 N/s and then oscillated in a sinusoidal wave form. The minimum to maximum load ratio, R', was kept equal to 0.1, and the frequency of the cyclic load was 3 Hz. Samples were gripped by serrated, flat faced hydraulic grips at a pressure of 10 MPa, in order to avoid slippage during loading. The free length between grips (gage length) was fixed at 35 mm. The fatigue life was arbitrarily set to an extension limit of 2 mm (5.7% strain). During the fatigue experiments, signals from the load cell and the LVDT channels were periodically recorded and analyzed, in order to determine the load displacement hysteresis loops and maximum specimen elongation.

3. Results and discussion

3.1. Static mechanical properties

The mechanical behavior of crosslinked and non-crosslinked unidirectional and filament wound compacts was studied before by our group, underlining the issue of crosslinking at the fused fiber skin [10,12]. Here, additional results are presented – mainly of the transverse and interlaminar shear properties of unidirectional compacts – to complete the picture and to supply sufficient background for the investigation of the dynamic behavior of UHMWPE fiber compacts. Table 1 displays the complete set of mechanical properties, including some previously published values, showing that the longitudinal flexural properties of UHMWPE fiber compacts were improved by an order of 20% through crosslinking [10]. It is seen that as a rule the mechanical properties of the crosslinked compacts are higher than those of the non-crosslinked ones. Crosslinking has two mutually dependent consequences that are manifested in the nature of the fiber–fiber contact region. On the one hand, it produces a network of covalent bonds between the fibers, which, on the other, retains the amorphous structure of the molten fiber skin and prevents its recrystallization upon cooling.

As expected, crosslinking improves the fiber coalescence that controls the transverse and shear properties. Moreover, it also improves the stress transfer mechanism that controls the longitudinal properties in the fiber dominated direction. In the transverse direction, the largest effect is seen for the transverse and shear yield strengths; the smallest effect is seen for the transverse modulus. Hence, in this direction, which is controlled by the properties of the newly formed matrix, crosslinking is more effective than crystallinity in its effects on the ultimate properties, while it is equivalent to crystallinity in its effect on the rigidity. In the fiber direction, where the efficiency of the stress transfer mechanism is critical to the static properties, crosslinking is more effective than crystallinity.

3.2. Dynamic mechanical properties

Having identified the dual consequences of crosslinking on transverse and longitudinal properties, we turn to investigate the dynamic behavior of the filament wound compacts. Fig. 1 introduces for general impression a scanning electron micrograph of a cross-section of a filament wound compact, marking the fiber and loading directions and the winding angle. Plots of the storage

Table 1
Mechanical properties of crosslinked and non-crosslinked, unidirectional UHMWPE fiber compacts

Materials	Flexural				Tensile				Interlaminar shear	
	Transverse		Longitudinal		Transverse		Longitudinal			
	Young modulus (GPa)	Stress at yield (MPa)	Young modulus (GPa)	Stress at yield (MPa)	Young modulus (GPa)	Stress at yield (MPa)	Young modulus (GPa)	Stress at yield (MPa)	Young modulus (GPa)	Stress at yield (MPa)
PE fiber compact	2.02	13.4	27.7	98	0.41	3.7	11.21	193	9.1	5.8
XLPE fiber compact	2.16	14.9	33.4	120	0.43	5.0	14.81	236	13.4	8.4

modulus (E') and the loss modulus (E'') against temperature at different frequencies for non-crosslinked and crosslinked filament wound compacts, respectively, are presented in Fig. 2(a) and (b). The typical relaxation peaks α, α′, β and γ are identified. The main difference between the non-crosslinked and the crosslinked materials is the absence of a significant β transition in the latter. Another minor difference is the ostensible appearance of a small α′ transition at high frequencies in the crosslinked compacts.

The molecular processes that are involved in the β relaxation are reasonably consensual, although they are still partially unclear. The relaxation is usually associated with motion of loose folds at the lamella surface, which are more common in branched PE, thus, requiring mobility of chains close to branch points. Hence, the intensity of the transition increases as the fraction of the material contained in partially ordered crystallite interface increases. It has been suggested that this is why thermal treatment (annealing in the solid state) of HDPE to increase its crystallinity generated significant β relaxation [3,4].

The latter observation is even more pronounced for the β relaxation in transcrystalline PE, characterized by a dense, highly ordered lamellar structure [3]. We have discovered a significant transcrystalline related β relaxation in UHMWPE fiber-reinforced HDPE (PE/PE composites). The β relaxation was identified first by dynamic mechanical analysis of PE/PE composites, where thermally treating the material to enhance transcrystallization increased the magnitude of the β peak significantly. A more recent study was performed by broadband dynamic dielectric spectroscopy applied to photo brominated/oxidized PE fiber in PE/PE composites. The fiber treatment increased the nucleation density of the HDPE matrix on its surface and produced a denser more ordered transcrystalline layer. As a result, a significant β relaxation was detected over a wide frequency range [4].

The results in Fig. 2 express the dual consequences of the crosslinking process at the coalesced fiber skins. At the processing temperature (145 °C) most of the forming molten matrix is amorphous while the fiber core remains in its original extended chain crystalline structure. A possible source of loose folds is the folded chain crystalline structure which may form upon transcrystallization of the forming matrix [3,4] and which crosslinking does prevent due to reduction of chain mobility.

The α relaxation above 50 °C is associated with an inter-lamellar shear process and is often separated into two processes, α and α′, with different activation energies – probably because of inhomogeneous crystallinity (the α′ transition is specifically attributed to intra-crystal lattice retardation phenomenon) [2]. It is evident in Fig. 2 that as the frequency is increased the position of the α transition moves to a higher temperature,

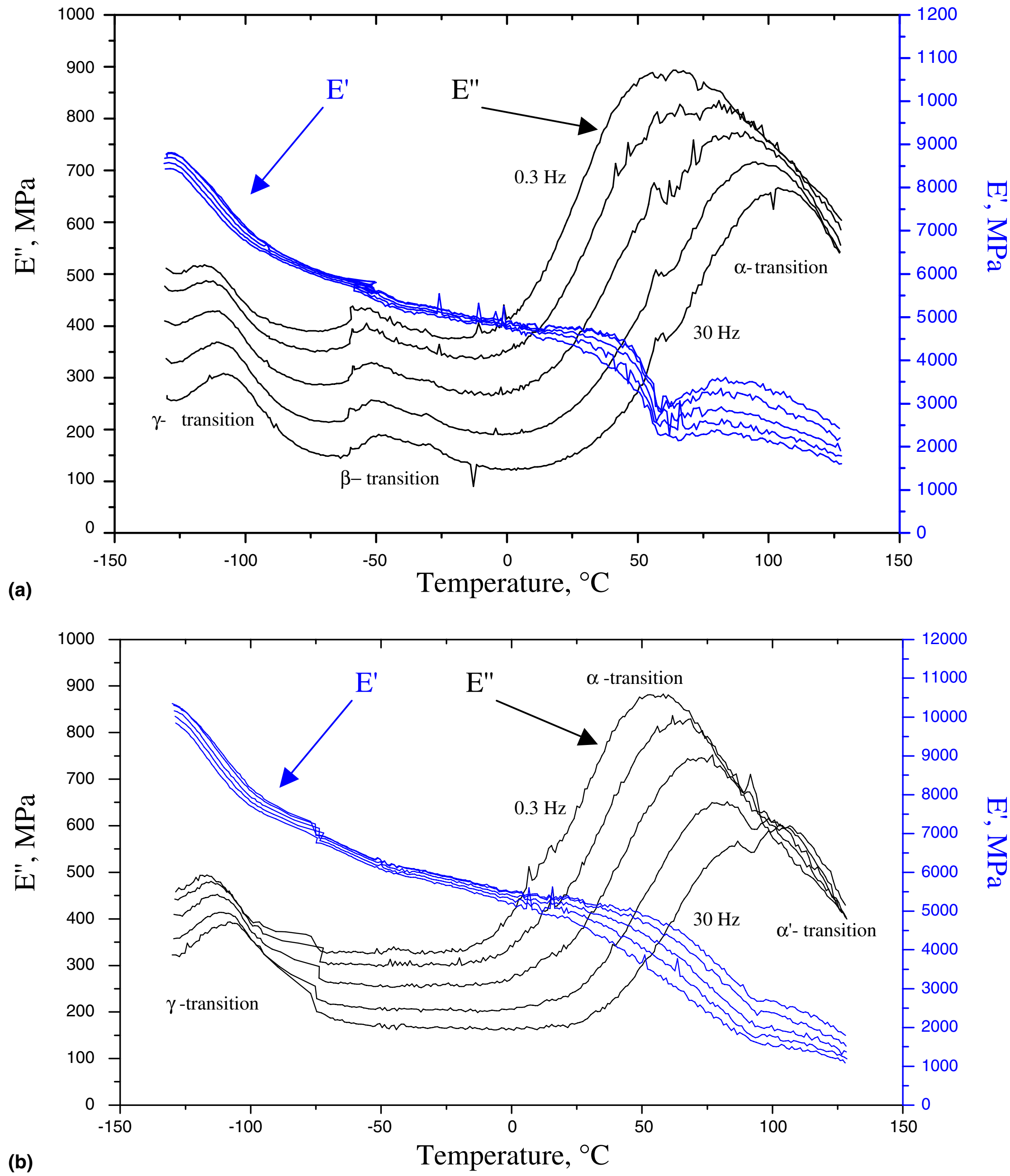

Fig. 2. Tensile storage and loss modulus as a function of temperature at different frequencies for (a) non-crosslinked and (b) crosslinked filament wound compacts.

indicating that the polymer chains need more energy to respond to the shorter timescale stresses imposed at higher frequencies. The reason of apparent small α′ transition at high frequencies in the crosslinked compacts is not clear.

The crosslinked samples exhibit slightly higher storage modulus values (E') than the non-crosslinked ones, in agreement with previously reported results [10,12]. For example, the room temperature values at 30 Hz are 4.7 and 4.4 GPa, respectively. It is concluded that the relative effectiveness of crosslinking versus degree of crystallinity regarding rigidity varies with the winding angle that in turn determines the loading angle with respect to the fiber direction (Fig. 1). It is expected that for low angles, where the matrix–fiber stress transfer mechanism is dominant, crosslinking is more effective, while the degree of crystallinity is more effective at high angles, where the matrix properties control those of the compact.

To complete the picture of dynamic behavior, unidirectional fiber compacts were tested in tension at right angle to the fiber direction. Fig. 3(a) and (b) presents plots of E' and E'' against temperature at different frequencies for non-crosslinked and crosslinked unidirectional compacts, respectively. In comparison with the filament wound samples, the transverse modulus of the unidirectional compacts exhibits threefold lower values. Here both the non-crosslinked and crosslinked samples exhibit a small β relaxation, observable only at high scale sensitivity. However, a valid quantitative comparison is impractical due to a low signal-to-noise ratio. As expected for high loading angles such as transverse loading of unidirectional composites, where the matrix properties control those of the compact, the effect of crosslinking is comparable to that of crystallinity, both of which reduce creep deformation. Hence, similar transverse storage modulus values are obtained for crosslinked and non-crosslinked samples. For example, the room temperature values at 30 Hz are 2.1 and 1.8 GPa, respectively.

By assuming an Arrhenius type relationship between frequency and peak temperature the activation energies of the three relaxations were calculated by plotting the frequency against the reciprocal temperature [3]. The results of the filament wound compacts are presented in Table 2. As explained above, only in the non-crosslinked filament wound compact was it possible to calculate valid activation energy of the β relaxation. It is noted that in this one case the activation energy of the β relaxation is quite significant; in fact, it is higher than those of the α and γ relaxations. A significant β relaxation is in

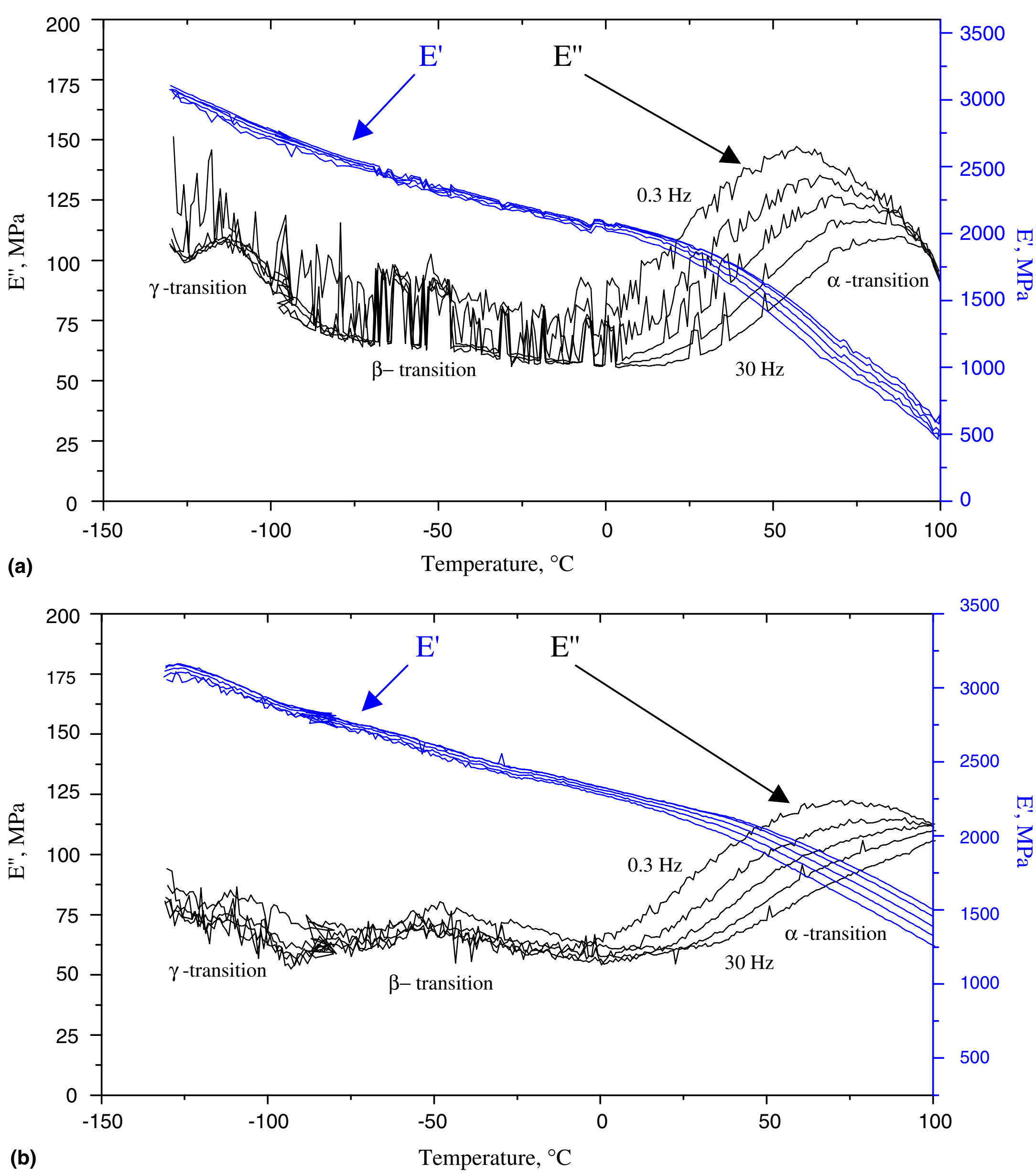

Fig. 3. Transverse tensile storage and loss modulus as a function of temperature at different frequencies for (a) non-crosslinked and (b) crosslinked unidirectional compacts.

Table 2
The activation energies of α, β and γ relaxations of UHMWPE filament wound compacts and composites

Filament wound material	Activation energy (kJ/mol)		
	γ	β	α
Crosslinked compact	138	–	158
Non-crosslinked compact	142	184	120
Thermally treated PE/PE composite [3]	88	248	412

agreement with our previous observations in the thermally treated filament wound PE/PE composites containing transcrystallinity. The average activation energy values of those PE/PE composites are also presented in Table 2. Further comparison between the present non-crosslinked filament wound compacts and the former filament wound PE/PE composites reveals that in the compacts the activation energy of the α relaxation, associated with the crystalline structure, is significantly lower while the γ relaxation, associated with the glass transition, is significantly higher. These differences are compatible with the fact that relative to the compacts the PE/PE composites contained a significantly higher volume of transcrystallinity as well as thermally treated crystalline matrix.

3.3. Fatigue behavior

The static and dynamic results provide us with specific information on the effect of crosslinking on the strength and modulus of the filament wound compacts. They also teach us how this effect depends on the loading direction with respect to the fiber. To complete the picture, a study of the fatigue behavior follows. Again, a comparison is made with our previous results of the fatigue behavior of the filament wound PE/PE composite [8,9]. Consequently, the same criterion for fatigue failure of 2 mm extension was chosen, which amounted to a fatigue strain limit of 5.7% – approximately half way between the static yield strain and the ultimate failure strain. At this strain limit, most of the specimens did not exhibit any visual damage.

Fig. 4 presents the fatigue results for crosslinked and non-crosslinked compacts (tested at 3 Hz frequency) plotted as stress/log$N$ graphs. It is clear that crosslinking offers significant advantage in terms of both the absolute stress and the rate of degradation. Due to the high winding angle, the damage is not fiber dependent [9] and occurs both at the matrix and at the interfacial region. Obviously, in this case crosslinking of the coalesced fiber skins improves the resistance to cyclic loading and damage propagation more than the alternative of matrix crystallinity. The unique fatigue performance of the filament wound compacts (even of the non-crosslinked structures) becomes obvious by comparing their performance with other filament wound homologues from our previous studies. Therefore, a comparison is made with PE/PE composites of UHMWPE fiber reinforced HDPE [8] and LLDPE [9]. The comparison is based on the values of the rate of degradation, which represent damage propagation, displayed in Table 3.

In addition to the absolute rate of degradation values, Table 3 presents the scaled values, obtained through dividing the fatigue stress by the static yield stress of the sample. It is obvious that the performance of the crosslinked compacts is by far better both in terms of absolute

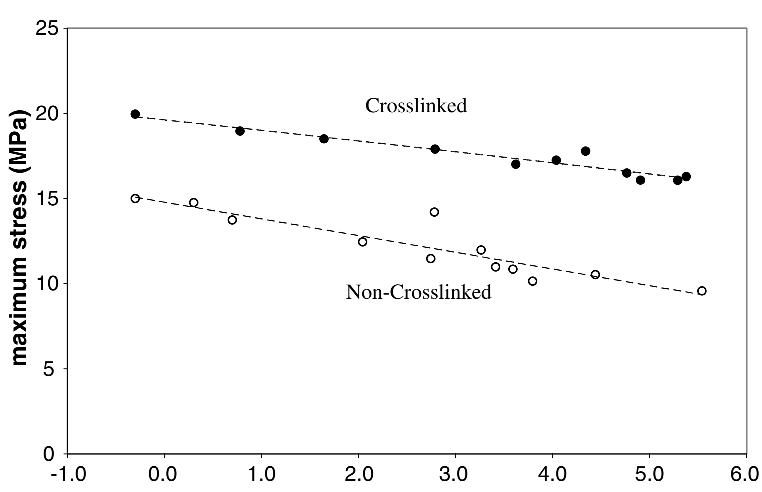

Fig. 4. Fatigue characterization of crosslinked and non-crosslinked UHMWPE compacts.

Table 3
Fatigue rate of degradation data of filament wound compacts and composites

Sample	Fatigue degradation rate (MPa) $(\log N)^{-1}$	Scaled degradation rate $(\log N)^{-1}$
Non-Crosslinked UHMWPE compacts (50°)	0.98	0.07
Crosslinked UHMWPE compacts (50°)	0.64	0.03
UHMWPE/HDPE composites (45°) [8]	4.5	0.11
UHMWPE/LLDPE composites (42°) [9]	2.8	0.06

and scaled values. This underlines the advantage of crosslinking in the coalesced fiber skin over matrix crystallinity or transcrystallinity, pertaining to ultimate static and fatigue properties at an angle to the fiber direction.

4. Conclusions

The analysis of the relaxation processes in UHMWPE fiber compacts shows clearly that crosslinking at the fiber–fiber coalesced interface that forms of the molten fiber skin in the compaction process, prevents transcrystallization and/or bulk crystallization in the new matrix. The study of static and fatigue behavior reveals that crosslinking is significantly more effective than transcrystallization in enhancing the ultimate properties. In the filament wound compacts, fatigued at an angle to the fiber direction, the scaled rate of fatigue degradation of the crosslinked structure is more than 50% smaller than the non-crosslinked counterpart and any of the PE/PE composite homologues.

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