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Elastic and viscoelastic behavior of filament wound polyethylene fiber reinforced polyolefin composites

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Filament wound flat strip composites of polyethylene fiber reinforced polyolefins are presented and studied. The versatility of this product is demonstrated by involving different polyolefin compositions based on ethylene-butene copolymers with a range of fiber volume fractions and various winding angles. The mechanical performance of the composite product agrees with standard theoretical predictions for angle-ply composites, while the dynamic mechanical analysis reflects the viscoelastic nature of the matrix. In particular, the branching density of the polyolefin backbone, expressed by the β-transition peak, dominates the dynamic mechanical behavior. The feasibility of a potential biomedical application is discussed based on process variable optimization, resulting in a specific combination of static and viscoelastic properties.

1. Introduction

Polyethylene (PE) composites with continuous fiber reinforcement of high volume fraction are known to possess impressive values of specific strength and stiffness. Besides this, different matrix materials and different production techniques, such as filament winding, allow to design composites with unique properties for different applications [1]. It is important to understand the effect of composition and process parameters, such as the matrix type, the angle of reinforcement and the fiber volume fraction, on the elastic and viscoelastic behavior of these structures.

In filament wound composites, fiber continuity plays a major role in determining the structural performance. Although most of the studies and applications of filament wound structures subject them to internal pressure [2–6], including studies of biomedical applications [7–9], a number of studies look into their axial tensile properties [10, 11]. Under axial tensile loading, filament wound structures exhibit a yield point followed by a draw region with fiber re-alignment in the loading direction. (In contrast, angle-by composites usually fail catastrophically by shear [12].) This special case of axial loading of filament wound structures widens their scope of application, offering new engineering and structural properties.

A useful tool for studying the effect of process and product variables on the performance is dynamic mechanical analysis (DMA), being highly sensitive to the inherent properties of the constituents and to their mutual interaction. Pertinent to the specific system of copolyolefins, DMA can reflect effects of branching density, degree of crystallinity and glass transition temperature, in reference to reported data in the literature. In fact, extensive information exists on phase transition of polyolefins detected by the temperature dependence of the loss tangent or the loss modulus [13], the effect of copolymers on the β transition [14–16], and on the relation between relaxation processes and tensile deformation of polyethylene [17]. It is generally accepted that high-density polyethylene (HDPE) exhibits two major transitions while low-density polyethylene (LDPE) exhibits three, including a β transition, attributed to branching. Both HDPE and LDPE exhibit a γ relaxation, occurring between -150°C and -110°C, due to the onset of short-range conformational changes in the amorphous regions and associated with the glass transition. The β relaxation is also thought to relate to the amorphous regions because its magnitude increases with decreasing of the crystalline fraction and the motion of very loose folds and relatively non-extended tie chains [18]. Therefore, it is more marked in LDPE and branched polyethylene below 0°C [13]. The α process both in LDPE and HDPE is a crystalline relaxation, attributed to shear of the chains within the lamellae activated by the rearrangement of the fold surface [16,17].

It has been shown that a relationship exists between the mechanical relaxation and the yielding behavior. At low temperatures PE fails in a brittle manner whereas at high temperatures it fails through strain softening with the formation of a neck. As the temperature is raised further, PE undergoes drawing and the neck propagates along the length of the sample [17].

The objective of this paper is to present and discuss a new type of filament wound, flat strip composites of polyethylene fiber reinforced polyolefins. It is intended to demonstrate the versatility of this product by involving different polyolefin compositions based on

ethylene-butene copolymers with a range of fiber volume fractions and various winding angles. The study will focus on the mechanical performance of the composite product and on how it is affected by the branching density of the polyolefin backbone and the viscoelastic nature of the matrix. The feasibility of a potential biomedical application will be evaluated based on material parameters such as the branching, winding angle and fiber volume fraction, resulting in a specific combination of static and viscoelastic properties.

2. Experimental

2.1. Materials

Composite materials were produced from Spectra 1000 UHMWPE fibers (Allied Signal) embedded in an ethylene-butene copolymer matrix of the Exact family (ExxonMobil). Three different copolymers were used, whose brochure data are presented in Table I. The copolymers were supplied in pellet form, from which 0.25 mm thick sheets were molded by pressing at 100°C under a pressure of 625 MPa (Carver Laboratory Press), followed by removing them from the press and cooling in an ice-water bath. Filament winding was performed using a bench winder (Burlington Instruments Co., Vermont) as described in [12]. A flat mandrel (2.5 mm wide, 0.5 mm thick and 135 mm long) was wrapped by a matrix film onto which the fiber was wound at a designated angle, and then wrapped by a second matrix film to produce a preform. The resulting preform was carefully removed from the mandrel and pressed at 100°C under 15 MPa for 30 minutes, followed by ice water cooling. Specimens of three winding angles of 28°, 32° and 42° were produced at a fiber weight fraction of about 0.65. The final strips were 4 mm wide by 0.4 mm thick. Fig. 1 presents examples of the preform and of the composite strip. (It is apparent that at this stage of our work the filament winding operation in still not sufficiently accurate to produce uniform fiber spacing.)

2.2. Testing

Axial tensile testing was carried out on an Instron universal tester with a loading gauge of 30 mm. The loading rate was 10 mm/min. The modulus and the yield stress in the loading direction x, E_x and σ_x were determined from the initial portion of the stress-strain curve.

Tensile dynamic mechanical tests were conducted under liquid nitrogen by a dynamic mechanical analyzer (DMA 983, TA Instruments). All the samples were tested in the temperature range from −150°C to 100°C, at a heating rate of 5°C/min, at a fixed frequency of 1 Hz.

TABLE I Characteristics of the polyethylene-butene copolymer matrices

Matrix	Branching (per 1000 main chain C atoms)	Yield stress (MPa)	Strain (%)	Modulus (MPa)	Crystallinity (%)
Exact 4041	66	1.5	27	22	10
Exact 4011		2.1	23	30	13
Exact 4015	42	2.8	22	42	17

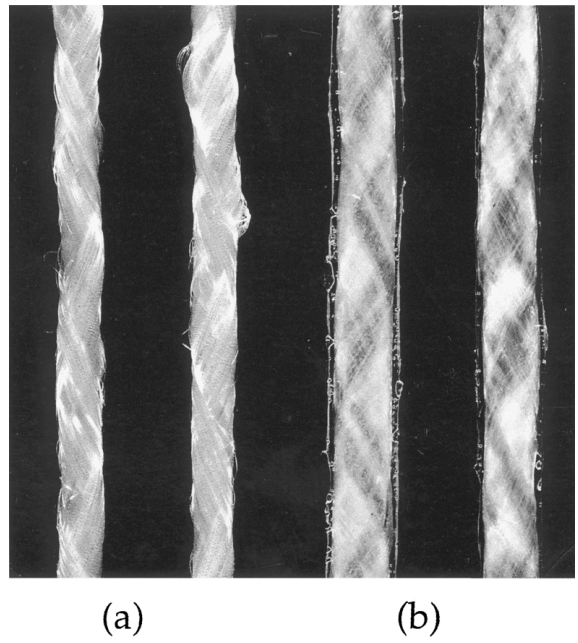

Figure 1 Pictures of (a) filament wound preforms and (b) composite strips.

3. Results and discussion

3.1. Axial tension

An advantageous characteristic of filament wound composite structures is that they offer a wide compliance range, controlled by the winding angle and the volume fraction of the fiber. Axial tension tests were performed to evaluate the effect of the winding angle on the mechanical properties of the composite. Fig. 2 shows the results of the engineering modulus, as a function of the angle θ between the axial and fiber direction. The experimental results are compared with a theoretical prediction for Exact 4011 composites strips based on a transformation of the principal elastic constants [19]. The compliance along the fiber direction, $1/E_x$, of an orthotropic lamina with its principle axis oriented at an angle θ with respect to the coordinate is expressed as follows:

$$1/E_x = (\cos^4\theta)/E_{\mathrm{L}} + (\sin^4\theta)/E_{\mathrm{T}} + 1/4(1/G_{\mathrm{LT}} - 2\nu_{\mathrm{LT}}/E_{\mathrm{L}})\sin^2 2\theta \quad (1)$$

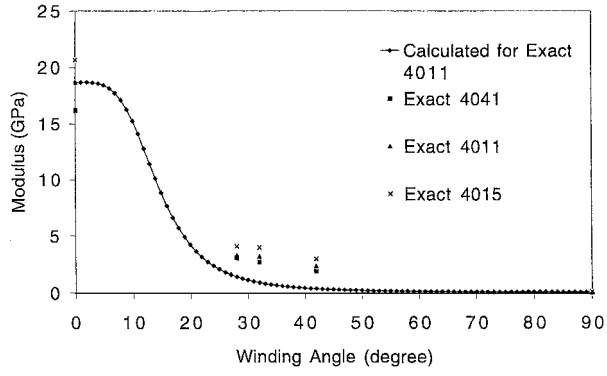

Figure 2 The engineering modulus as a function of the angle θ between the axial and fiber direction.

TABLE II Calculated and experimental axial tensile values for filament wound composites with 65% fibers

Properties	σ_T (MPa)	E_T (MPa)	σ_L (MPa)	E_L (GPa)	G_{LT} (GPa)	υ_{LT}
Exact 4041/PE	1.5	55	554	16.2	6.3	0.3
Exact 4011/PE	2.1	75	604	18.7	7.2	0.3
Exact 4015/PE	2.8	99	693	20.6	7.9	0.3

where E_x is Young's modulus in the axial direction, E_L, E_T, G_{LT} and υ_{LT} are the Young's moduli, the shear modulus and the Poisson ratio, respectively, of the composite lamina, and L and T denote the principal material axes (longitudinal and transverse). The calculation is based on the extrapolated values of E_L and E_T, and the calculated value of G_{LT} ($G_{LT} = E_L/[2(1+\upsilon_{LT})]$) and the estimated value of υ_{LT} is taken from the literature on PE/PE composites [20]. These values are given in Table II.

As expected, the variability of the modulus depends on the properties of the constituents. The stiffness of the composite may be controlled either by the modulus of the reinforcement or by that of the matrix, considering that the rigid component (the fiber) controls the stiffness in the longitudinal direction, while the compliant one (the matrix) does it in the transverse direction. As seen in Fig. 2, the modulus of the composite decreases with the branching density of the polyolefin matrix. For any given system, the stiffness depends on the loading angle [12]. This is reflected in the trends of the experimental results compared with that of Equation 1. It is noted that all the material parameters, which are included in Equation 1, are a function of the fiber volume fraction, which is not examined here, though.

The strength at an angle θ to the fiber direction is controlled by the mechanical properties of the matrix. Failure occurs by yielding, succeeded by matrix drawing and fiber re-orientation in the loading direction [2]. From an engineering standpoint, although matrix yielding controls the small strain behavior, the ultimate strength of the composite is controlled by the fiber, offering a kind of inherent safety factor. The yield stress is predicted by a number of failure criteria, based on different combinations of the main failure modes, namely longitudinal, shear and transverse. Considering the transformations that express the main stress components of an axial stress, σ_θ, the failure strength predicted by the maximum stress theory [19] is obtained from the smallest value of the following stresses:

$$\begin{aligned} \sigma_\theta &= \sigma_L/\cos^2\theta \\ \sigma_\theta &= \tau_{LT}/\sin\theta\cos\theta \\ \sigma_\theta &= \sigma_T/\sin^2\theta \end{aligned} \qquad (2)$$

where σ_L, τ_{LT} and σ_T are the ultimate longitudinal, shear and transverse stress, respectively. Fig. 3 presents the experimental results of the three systems plotted against θ and compared with the maximum stress criteria for the Exact 4011 composite system. The values of σ_L, τ_{LT} and σ_T used in the calculations, are the average

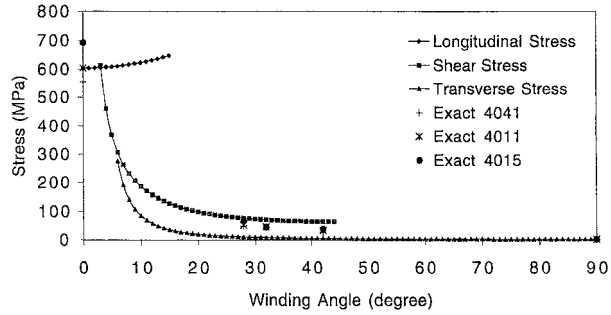

Figure 3 The ultimate tensile strength as a function of the angle θ between the axial and fiber direction: a comparison with the maximum stress failure criterion.

experimental values obtained for $\theta = 0$, 42 and 90°, respectively (Table II). It is seen that the experimental yield stresses correspond to the third failure regime, which is governed by the transverse failure mode. In this failure regime the angle effect is relatively moderate.

3.2. Dynamic mechanical experiments

Dynamic mechanical tests (DMA) measure the response of a material to a periodic stress, and they give, in general, more information about a material than other mechanical property tests. Dynamic tests over a wide temperature range are especially sensitive to the chemical and physical structure of polymers and for studying glass transitions and secondary transitions in amorphous as well as the morphology of crystalline polymers. The (dynamic) modulus is a basic mechanical property, important in any structural application while mechanical damping is a sensitive indicator of molecular motions.

DMA tests were performed in this study to characterize the polyolefin copolymer composites. The real (E') and loss modulus (E'') results were examined and all transition peaks were automatically picked by the DMA program. As expected, they display a strong dependence on material parameters such as the branching, winding angle and fiber volume fraction. The trends correspond with the above elastic modulus data obtained by axial quasi-static tension. The results are presented in Figs 4–9, where the material parameters are considered separately: the matrix (Figs 4 and 5), winding angle (Figs 6 and 7) and fiber volume fraction (Figs 8 and 9).

The real modulus at 24°C for a winding angle of 42° increases from 5.1 to 11.2 GPa as the branching of the matrix decreases from 66 to 42 branches per 1000 backbone C atoms (Fig. 4); to 14.1 GPa as the fiber volume fraction is increased from 65 to 81% (Fig. 8); and to 21.8 GPa as the winding angle is decreased from 42° to 28° (Fig. 6). These observations are consistent with the theoretical prediction for Young's modulus of composite materials, predicting increased stiffness for higher matrix rigidity and fiber alignment and volume fraction.

The imaginary modulus (Figs 5, 7 and 9) expresses the various phase transitions as described above. The γ relaxation, which corresponds to the glass transition, exhibits small variations around −120°C for the

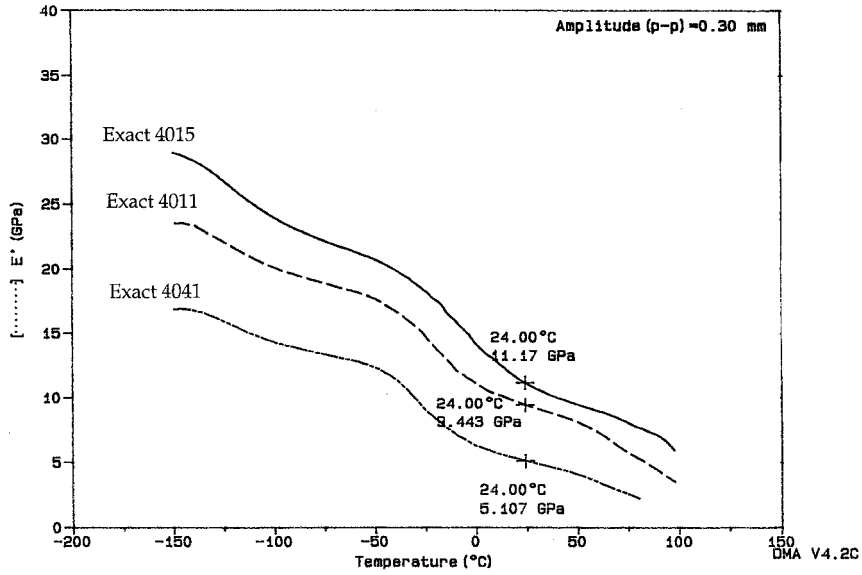

Figure 4 DMA results of the real modulus for the three copolymers for a constant winding angle and fiber content of 42° and 65%, respectively.

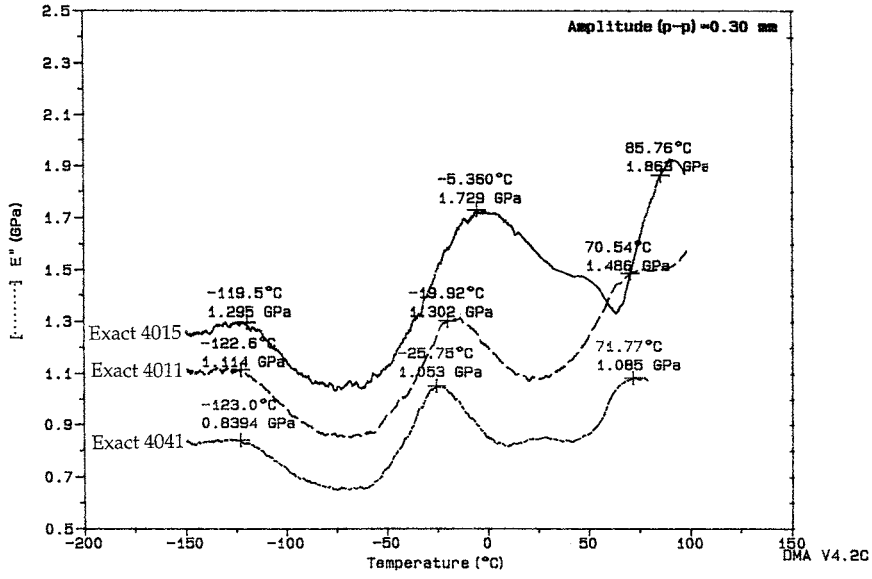

Figure 5 DMA results of the imaginary modulus for the composites of Fig. 4.

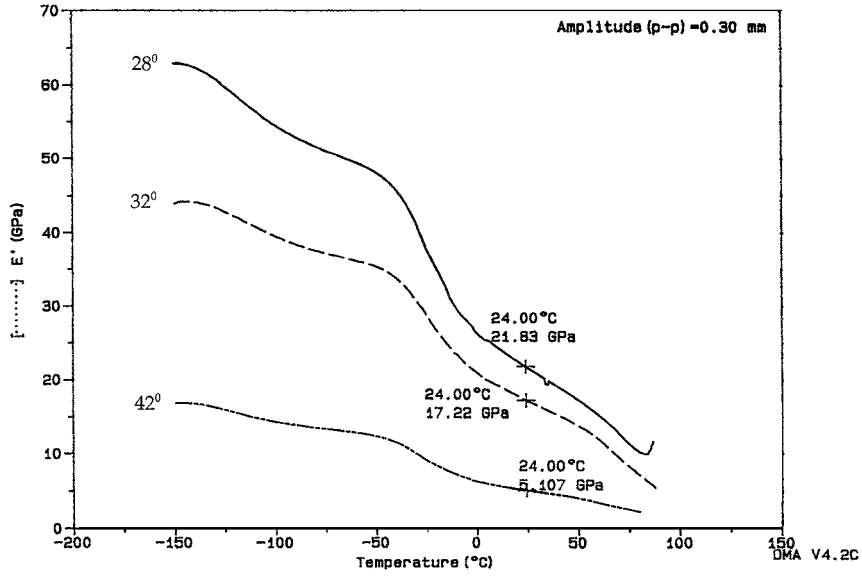

Figure 6 DMA results of the real modulus for Exact 4041 composites of different winding angles and a constant fiber volume fraction of 65%.

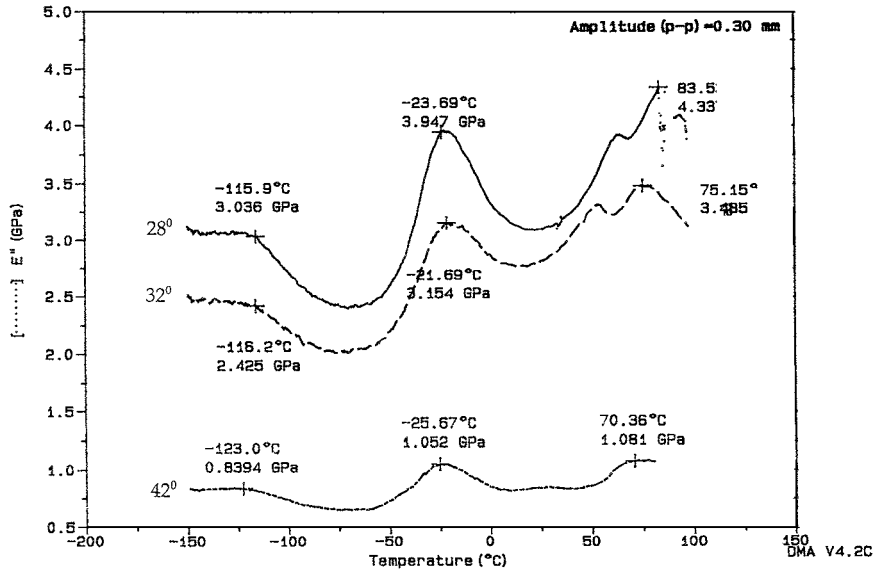

Figure 7 DMA results of the imaginary modulus for the composites of Fig. 5.

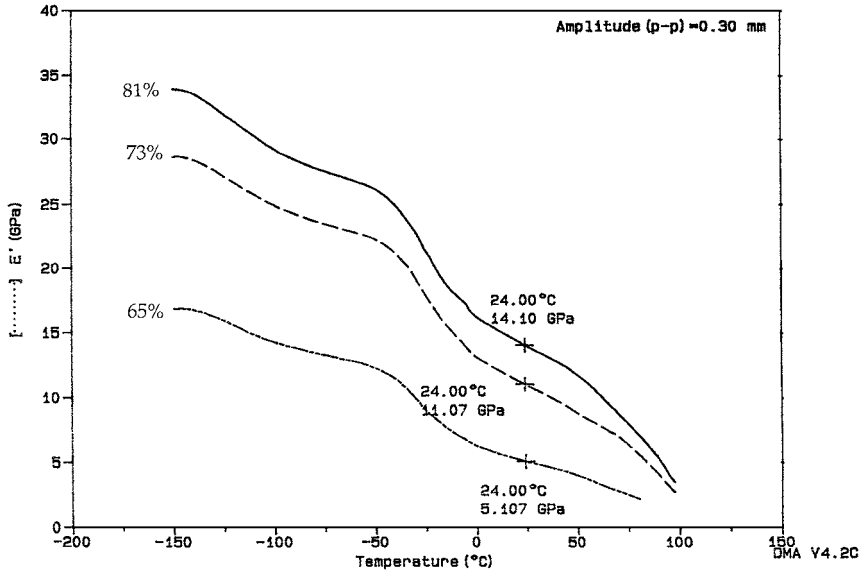

Figure 8 DMA results of the real modulus for Exact 4041 composites of different fiber volume fractions and a constant winding angle of 42°.

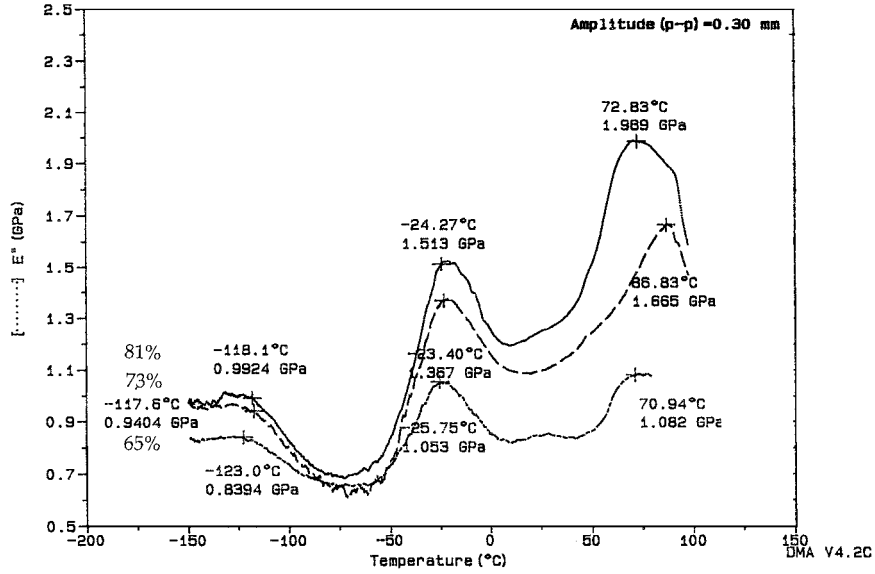

Figure 9 DMA results of the imaginary modulus for the composites of Fig. 5.

different material parameters. It has been shown that an increase in crystallinity owing to decrease in branching leads to a shift of the γ relaxation towards a higher temperature [15]. This is evident in Fig. 5, where a gradual shift from -119.5°C to -122.6°C and -123.0°C is observed with the crystallinity of the copolyolefins. The magnitude of the γ peak follows a similar order, increasing from 0.8 to 1.1 and 1.8 GPa.

The α relaxation peaks, associated with the crystalline phase [15], and specifically with the crystal thickness [16], exhibit an inconsistent trend in the range 70°C to 86°C, resulting probably from the low percentage of crystallinity in the copolymer matrices. However, the magnitude of the α relaxation peaks depends on the branching, decreasing from 1.9 to 1.1 GPa as the branching density is increased (Fig. 5). This has been attributed to a reduced degree of crystallinity associated with the higher content of comonomer [15].

The most interesting observation concerns the β relaxation in the temperature range -26°C to -5°C. Although, the origin of this process is still unresolved, it is commonly attributed to motions in the amorphous region. Because in LDPE the β relaxation is a dominant process while in HDPE it is an insignificant one, it has been associated with motion of side chains [13, 14]. This is reflected in the results in Fig. 5 for the copolyolefins, showing a significant β transition in the three copolymers, which is decreasing with the branching density from 1.7 to 1.1 GPa. The peak temperature of the β relaxation also reflects the branching density, varying from -5°C to -26°C. It has been shown in the literature that the β relaxation peak shifts to higher temperatures for bulkier side chains [15]. In this study, the β peaks shift to higher temperatures with decreasing the ratio of ethylene/butene. It is noted that the relative intensity of the β transition, e.g., the ratio of β/α, does not exhibit a consistent trend with the branching density.

The effects of the other material parameters, namely of the winding angle and the fiber content, on the relaxation peaks are such that as the fiber becomes more dominant the viscoelastic nature of the composite is reduced. Hence, the magnitude of the β transition peak increases with decreasing the winding angle from 1.1 to 3.9 GPa for 42° to 28°, respectively (Fig. 7), and from 1.1 to 1.5 GPa as the fiber volume fraction is increased from 65 to 81%, respectively (Fig. 9).

The tensile testing and the DMA results suggest that a material parameter optimization considering constituent and structural properties, such as matrix stiffness, winding angle and fiber volume fraction, may result in a specific combination of static and viscoelastic properties. A subsequent research is currently pursued to evaluate the feasibility of a potential biomedical application corresponding to a specific combination of static and viscoelastic properties. For example, the idea of tendon or ligament prostheses presented in reference [12] can be re-evaluated on the basis of various copolyolefin compositions.

4. Conclusion

This paper presents a new type of filament wound, flat strip composite of polyethylene fiber reinforced polyolefins. The versatility of this product is demonstrated by experimenting with different polyolefin compositions based on ethylene-butene copolymers, with a range of fiber volume fractions and various winding angles.

The effects of material parameters, in particular the branching density of the polyolefin backbone and the derived viscoelastic nature of the matrix, on the elastic and viscoelastic behavior of the filament wound composite strip are evident. Dynamic mechanical analysis reveals a significant β transition, which is related to the branching in the copolymer, for the three tested compositions. Increased branching shifts the β transition (and the glass, γ, transition) to lower temperatures and decreases the magnitude of the peak. These transitions also reflect the room temperature mechanical properties of the polymer, which are reflected, in turn, in the yield stress and Young's modulus of the composite structure.

It is concluded that the scope of material parameter combinations is wide and that optimization could deliver a product of potential biomedical feasibility.

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