Flexural and interlaminar mechanical properties of unidirectional liquid crystalline single-polymer composites

Alessandro Pegoretti *, Andrea Zanolli, Claudio Migliaresi

Department of Materials Engineering and Industrial Technologies and INSTM Research Unit, University of Trento, via Mesiano 77, 38050 Trento, Italy

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Abstract

New single-polymer composites were obtained by combining two types of wholly aromatic copolyester liquid crystalline fibres having melting points differing by about 40 °C. Vectran® M and HS fibres were co-wound on an open square metal frame in order to obtain a unidirectional preform with an equal volume fraction of both fibres. In a second stage, the preform was consolidated under pressure at temperatures ranging from 260 up to 285 °C. Under the selected processing conditions, one component (Vectran® M) formed a continuous matrix while the other one (Vectran® HS) retained its fibrous form and most of the original mechanical properties.

In the longitudinal direction, the bending modulus resulted to be substantially independent of the consolidation temperature ($T_c$) with an average value of about 39 GPa, while the maximum stress sustained in the outer layer increased from 157 MPa, at $T_c = 260$ up to 259 MPa, at $T_c = 285$ °C. Concurrently, all the matrix related properties such as the transversal bending modulus, the transversal maximum stress in the outer layer, and the interlaminar shear strength (ILSS) markedly improved as the consolidation temperature rose. In particular, both the maximum transversal bending stress and ILSS values increased by a factor of 2.8 as $T_c$ increased from 260 up to 285 °C. Moreover, the consolidation temperature resulted to slightly affect the Charpy impact resistance of the investigated composites that, up to $T_c = 280$ °C, oscillated around an average value of 79 kJ/m². On the other hand, the consolidation temperature markedly influenced the energy absorbing mechanisms. In fact, the ductility index showed a maximum value of 9 at $T_c = 265$ °C and then it monotonously decreased down to a minimum value of 4.5 at $T_c = 285$ °C.

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1. Introduction

Single-polymer composites consist of a matrix and fibres of the same chemical composition. Over the past 30 years, this concept has been extensively investigated with polyethylene [1–35]. More recently, some attempts have been also made with other polymers like polypropylene [36–42], poly(ethylene-terephthalate) [43–45], poly(ethylene-naphthalate) [46], and liquid-crystalline copolyesters [47–49].

Copolymers of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) with the following formula

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
x & \quad y
\end{align*}
\]

are the basis of the liquid-crystal engineering resins commercialized in 1985 by Hoechst Celanese Corporation (USA) under the trade name of Vectra®. Since 1986, Hoechst Celanese and Kuraray Company Ltd. (Japan) have jointly evaluated these materials in fibre applications. Vectra®


* Corresponding author. Tel.: +36 0461 882452; fax: +39 0461 881977. E-mail address: alessandro.pegoretti@ing.unitn.it (A. Pegoretti).

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high-performance fibre is produced from the Vectra® LCP [50] with a HBA/HNA molar ratio of 73/27 [51–53]. At present, the only examples of single-polymer composites consisting of liquid crystalline polymer (LCP) available in the scientific literature are the works of Hine and Ward [47,48] and of Stellbrink et al. [49], both focused on the hot-compaction of polyester–polyarylate Vectra® fibres.

In the hot-compaction process, a fraction of the surface skin of an array of oriented polymer fibres or tapes is melted under relatively low contact pressure and the structure is then consolidated by the application of a substantially higher pressure for a short time [48,54]. On cooling, the recrystallized polymer acts as a binder, like the resin matrix in a conventional heterogeneous composite. Ward and Hine firstly reported on the preparation of LCP unidirectional [47] and plane-weave [48] single-polymer composites by hot-compaction of Vectra® HS fibres. For unidirectional hot-compacted LCP single-polymer composites elastic moduli of 97.2 and 3.24 are reported for the longitudinal and the transversal directions, respectively [47]. For plane-weave Vectra® based composites tensile modulus and strength values of 7 and 0.13 GPa, respectively, are reported [48]. The hot-compaction of Vectra® HS filament-wounded preform has been also investigated by Stellbrink et al. [49]. At an hot-compaction temperature of 290 °C they were able to obtain 0/90° cross-ply laminates with tensile modulus and strength values as high as 33.3 and 0.616 GPa, respectively. The use of temperature and pressure to control the melting of the outer surface layer of polymeric fibres implies that the processing window for the hot-compaction process is quite narrow and this may constitute a problem for the industrial transfer of this technology. Moreover, with this approach it is very difficult, if not impossible, to preserve the original mechanical properties of the polymeric fibres.

In the first part of this paper, we introduced a new method for the production of single-polymer composites based on liquid-crystalline wholly aromatic copolymers Vectra® fibres [55]. Unidirectional composites have been obtained with two different commercial Vectra® fibres, as-spun or thermally treated, characterized by markedly different melting points. A processing window of about 40 °C allowed us to successfully adopt a co-woven/hot consolidation process for the composites production. Both longitudinal and transversal tensile mechanical properties resulted to be markedly dependent on the consolidation parameters such as temperature and pressure [55].

In this paper, we report on the effects of the consolidation temperature on the flexural and interlaminar properties of Vectra® based LCP single-polymer composites.

2. Experimental

2.1. Materials and composites preparation

Composites were prepared using two different commercially available Vectra® fibres, and namely:

- Vectra® M, linear density of 750 denier (1 denier = 9 g/km), 150 filaments per yarn;
- Vectra® HS, linear density of 1500 denier, 300 filaments per yarn.

These fibres have the same chemical composition, as revealed by the FT-IR spectra reported in Fig. 1, but markedly different properties. A detailed description of the main thermomechanical properties of these fibres is reported in the first part of this paper [55], and some data are briefly summarized in Table 1. Optical micrographs of polished transversal cross-sections of both type of fibres are reported in Fig. 2. Both fibres appear to have an almost circular cross-section. The diameter measured on 250 fibres results to be 25.5 ± 2.1 μm for Vectra® M and 25.1 ± 2.1 μm for Vectra® HS. These values are in good agreement with the microscopic observation previously performed along the fibre axis [55].

The preparation of the composites is carefully described in the first part of this paper [55], and it can be briefly summarized as follows. Both Vectra® M and HS fibre were co-wounded on a open metal frame (see Fig. 3a). The adopted winding sequence, that is represented in Fig. 3b, consisted of twelve winding passages purposely chosen in order to reach an equal volume fraction of both Vectra® M and HS fibres. The wounded preform was then inserted between the plates of a Carver Laboratory Press.

![Fig. 1. FT-IR spectra of Vectra® M and HS fibres.](image)

Table 1
Some properties of Vectra® M and HS fibres (taken from [55])

<table>
<thead>
<tr>
<th>Property</th>
<th>Vectra® M</th>
<th>Vectra® HS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temperature [°C]</td>
<td>276</td>
<td>315</td>
</tr>
<tr>
<td>Tensile modulus [GPa]</td>
<td>83.7</td>
<td>88.8</td>
</tr>
<tr>
<td>Weibull scale parameter [MPa]</td>
<td>1309</td>
<td>3374</td>
</tr>
<tr>
<td>Weibull shape parameter</td>
<td>8.28</td>
<td>6.13</td>
</tr>
</tbody>
</table>

| Notes | |
|-------| |

a Measured by DSC analysis.

b Values extrapolated from data obtained on single fibres tested at various gage lengths.

c Referred to a 25 mm gage length.
and consolidated according to the processing scheme described in Fig. 4. When a consolidation temperature $T_c$ was reached, the pressure was rapidly increased up to 4.4 MPa for a short period of 30 s. In this work the consolidation temperature was changed in the range from 260 up to 285 °C and the resulting composite sheets presented thickness values in the range from 2.45 to 1.89 mm, depending on the consolidation temperature.

2.2. Testing procedures

Three point bending tests were conducted in accordance to the ASTM standard D790 on bars of rectangular cross-section resting on two supports and centrally loaded by means of a loading nose. Specimens 90 mm long and 15 mm wide were obtained along both the longitudinal and the transverse directions. A span length of 76 mm assured a span-to-depth ratio of at least 30, and a cross-head speed of 32 mm/min was adopted. Tests were performed at room temperature with an Instron 4502 universal testing machine on at least three specimens for each sample. Longitudinal specimens were tested with a 1 kN load cell, while transversal specimens were tested with a 0.1 kN load cell.

Short beam shear tests were performed on small bars of rectangular cross-section. Specimens 36 mm long and 12 mm wide were machined out of the composite plates along the longitudinal directions. A span length of 24 mm assured a span-to-depth ratio lower than 13. Tests were performed at room temperature under a cross-head speed of 1 mm/min. The Instron 4502 universal testing machine was equipped with a 1 kN load cell.

Charpy impact tests were performed on test bars of rectangular cross-section, 90 mm long and 7 mm wide. Thinner specimens for the impact tests were prepared by limiting the winding sequence to the IV step, that provided sheets thickness after consolidation in the range from 0.82 to 0.67 mm [55]. Tests were performed by a Charpy instrumented pendulum CEAST model 6549. Specimens were supported to the machine anvils at a span length of 40 mm and broken by a single swing of the pendulum with the impact line midway between the supports in the flatwise direction. The striking nose of the pendulum was charac-
melt the Vectran/C210 appears that the matrix made of Vectran
higher magnifications (Fig. 5, b1 and b2) it clearly
Vectran low to induce any hot-compaction phenomenon among
HS fibres. Moreover, the consolidation temperature is too
the investigated consolidation temperature. At the same
time, it clearly emerges that Vectran® M fibres completely
loose their fibrous structure even at the lowest consolidation
temperature of 265 °C. On the other hand, the optical
micrographs of composites compacted at 260 and
265 °C indicate that the adopted temperature is too low
to obtain a satisfactory consolidation process. In fact, a
number of macro cracks located inside the original Vectran® HS yarns can be observed (Fig. 5, a1 and a2). At
higher magnifications (Fig. 5, b1 and b2) it clearly
appears that the matrix made of Vectran® M molten
fibres is not able to flow and efficiently bind the Vectran®
HS fibres. Moreover, the consolidation temperature is too
low to induce any hot-compaction phenomenon among
Vectran® HS fibres. At consolidation temperatures of
270 °C or higher, the micro cracks practically disappear
and the Vectran® HS fibres seem to be quite homogeneously bounded by the Vectran® M matrix. Nevertheless,
it is worthwhile to note that Vectran® M matrix is not
able to flow in the intertices between the Vectran® HS
fibres, but it rather plays as a binder between the individual Vectran® HS yarns. The optical micrographs indicate
that a consolidation temperature of 265 °C is enough to
melt the Vectran® M matrix but not to force it to flow
between the individual Vectran® HS fibres that com-
pletely maintain their original shape. At 280 °C Vectran®
M matrix partially flows and bind the Vectran® HS fibres
that also appear to be slightly deformed in correspond-
ence of the points of contacts.

The observed changes in the microstructure are also
accompanied by macroscopic changes in the composite
sheets, such as variations of their thickness, that markedly
decreases as the consolidation temperature rises (see
Fig. 6). Interestingly enough, the sheet thickness appears
to be practically independent of the consolidation tempera-
ture up to 270 °C, and then it linearly decreases with the
consolidation temperature. This behaviour can be inter-
preted by considering that for temperatures higher than
270 °C the Vectran® M molten fibre assume a viscosity suf-
ficiently low to flow and to be partially squeezed out of the
composite plates. The Vectran® HS fibre volume fraction
can be estimated by assuming that its value is 0.5 at the
lowest consolidation temperature, and that the thickness
variations can be attributed to a flow of Vectran® M
matrix out of the composite sheets. Under this hypotheses
it is possible to compute that Vectran® HS fibre volume fraction is increasing up to 0.65 with the consolidation tem-
perature in the way reported in Fig. 6.

3. Results and discussion

3.1. Composites microstructure

The optical micrographs of un-etched polished cross-
sections of composites consolidated at various tempera-
tures are collected in Fig. 5 at various magnification
levels. First of all, it is interesting to note that Vectran®
HS fibres maintain their fibrous morphology at each of
the investigated consolidation temperature. At the same
time, it is worthwhile to note that Vectran® M fibres completely
loose their fibrous structure even at the lowest consolida-
tion temperature of 265 °C. On the other hand, the optical
micrographs of composites compacted at 260 and
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it is possible to compute that Vectran® HS fibre volume fraction is increasing up to 0.65 with the consolidation tem-
perature in the way reported in Fig. 6.

3.2. Three point bending test

The modulus and maximum stress sustained in the outer
layer, as measured by three-points bending tests on speci-
mens with the main axis oriented along the fibre direction,
are reported in Fig. 7 as a function of the consolidation
temperature. It is seen that the bending modulus is substan-
tially independent of the consolidation temperature with an
average value of about 39 GPa. Uniaxial tensile tests per-
formed on thinner composite plates of the same composi-
tion indicated markedly higher modulus values [55]. In
fact, up to 280 °C the tensile modulus resulted to be scar-
cely affected by the consolidation temperature with an
average value of about 59 GPa. This wide discrepancy
could be attributed to the following factors. First of all,
an anisotropy in the tensile/compressive mechanical behav-
iour of Vectran® fibres may be assumed. In fact, even if no
experimental information are available for Vectran® fibres,
there are several experimental evidences that highly ori-
ented fibres behave in a different manner if loaded under
tension or compression [56,57]. In fact, by Raman spectros-
copy on PAN-based carbon fibres, Melanitis and Galiotis
were able to evaluate that the ratio of the compressive to
tensile moduli can change in the range from 0.96 down
to 0.68 depending on the fibre type [56]. In a more recent
study on Kevlar 49 fibre, Dobb and Ghane reported a
value of 0.72 for the ratio of the compressive to
tensile moduli [57]. In the bending tests a part of the specimen is
actually subjected to compressive loads and, consequently,
the estimated modulus could be affected by the fibre anisot-
ropy, if any. Another factor that could account for the
lower bending modulus with respect to tensile one is the

![Fig. 4. Schematic of the processing temperature and pressure profiles.](image-url)
effect of the shear deformation that is always present in the bending configuration. This component is more and more important as the span-to-depth ratio diminishes and, if neglected, it usually yields to apparent bending moduli lower than those measured under uniaxial tension. In order to overcome this problem, ASTM D790 standard recommends a span-to-depth ratio of at least 16 for homogeneous materials and it also claims that for some highly anisotropic composites, shear deformation can significantly influence modulus measurements, even at span-to-depth ratio as high as 40. In the present case, the span length is 76 mm that corresponds to a span-to-depth ratio in the range from 31 up to 40, depending on the plate thickness.

In the bending tests the maximum normal stress reached in the outer layer is usually considered as a measure of the material strength. The effect of the consolidation temperature on the maximum stress in the outer layer is also reported in Fig. 7. It is important to consider that, in the present case, the bending of composite specimens do not provoke the tensile or compressive failure of the outer layers but a load drop occurs when an interlaminar crack starts and propagates. As a consequence, the reported maximum stress values could be

Fig. 5. Optical micrographs of the un-etched polished cross-sections of composites consolidated at 260 °C (a1, a2), 265 °C (b1, b2), 270 °C (c1, c2), 275 °C (d1, d2), 280 °C (e1, e2), and 285 °C (f1, f2).
related to the interlaminar shear strength rather than the longitudinal tensile strength. In fact, the strength values measured under tensile mode resulted to decreases from 920 to 480 MPa when the consolidation temperature increased from 265 to 285 °C [55]. On the contrary, the maximum bending stress reported in Fig. 7 is increasing with the consolidation temperature, with a trend typical of the matrix related properties, such as the transversal strength [55].

The bending modulus and maximum stress values measured on specimens with fibres transversally oriented are reported in Fig. 8. Similarly to the transversal tensile modulus and strength [55], also modulus and maximum stress values are increasing with the consolidation temperature. It can be noticed that an improvement of a factor 2.8 of the transversal maximum stress is observed when the consolidation temperature is raised from 265 up to 285 °C.

3.3. Short beam shear test

The load–displacement curves obtained from the bending tests of specimens with a low span-to-depth ratio are reported in Fig. 9 for several consolidation temperatures. In all cases, mid-plane interlaminar failure has been clearly observed. Consequently, the strength values determined

Fig. 5 (continued)
from this test method can be attributed to the interlaminar shear resistance. In particular, accordingly to the indications of the ASTM standard D2344, an interlaminar shear strength (ILSS) parameter has been computed from the maximum load observed during the test, $P_m$ according to the following equation:

$$\text{ILSS} = 0.75 \frac{P_m}{bh} \quad (1)$$

where $b$ and $h$ are the specimens width and thickness, respectively. ILSS values evaluated on the basis of Eq. (1) are reported in Fig. 10. The resistance to shear-induced delamination is profoundly affected by the consolidation temperature. In particular, as the consolidation temperature rises the ILSS values markedly increase from 3.9 MPa at 260 °C up to 10.8 MPa at 285 °C. It is interesting to observe that the parameter ILSS increases by a factor of about 2.8, that exactly corresponds to the variation of the maximum stress evaluated in the three-point bending test in the transversal direction.
3.4. Charpy impact test

A representative load–time curve as obtained from instrumented Charpy impact tests is reported in Fig. 11a. It is seen that the force increases reaching a maximum corresponding to the onset of failure. The fracture is not catastrophic but the crack propagation requires a certain amount of energy. Moreover, the visual inspection of the specimens after the impact test (see Fig. 11b) put in evidence that no complete breakage occurs, and that the energy absorbing mechanisms are related to extended delamination and splitting. A number of reinforcing fibres also appear to fail under tension on the outer composite layer. The cumulative energy during the impact test is represented on the same Fig. 11a. For each specimen, the Charpy impact resistance could be evaluated by measuring the total energy to fracture ($E_t$) and normalising it to the specimen cross-sectional area. $E_t$ can be seen as the summation of a crack initiation energy ($E_i$) and a crack propagation energy ($E_p$). Beaumont et al. [58] defined a dimensionless parameter called the ductility index (DI), which is found useful for ranking the impact performance of different materials under similar testing conditions. The DI is defined as the ratio between the propagation energy and the initiation energy, i.e.:

$$\text{DI} = \frac{E_p}{E_i} \quad (2)$$

High values of DI would mean that most of the total energy is expended for crack propagation. The Charpy impact resistance and the ductility index values are reported in Fig. 12 as a function of the consolidation temperature. The Charpy impact resistance is practically independent of the consolidation temperature up to 280 °C, oscillating around an average value of about 79 kJ/m². At a consolidation temperature of 285 °C a slight decrease to 64 kJ/m² is observed. These values are quite satisfactory if compared with the typical fracture energy data reported for traditional fibre reinforced polymer composites [59]. On the other hand the ductility index is negatively affected by a rise of the consolidation temperature, showing a maximum value of 9 at $T_c = 265$ °C and a monotonous decrease down to a minimum value of 4.5 at $T_c = 285$ °C. This trend could be tentatively explained by considering that the interlaminar shear strength increases with the consolidation temperature thus limiting the formation of delamination crack paths that are generally responsible of energy dissipation processes.

4. Conclusions

The hot-consolidation of co-wounded preforms offers a method for the manufacture of new single-polymer liquid crystalline composites. The flexural mechanical behaviour under static and impact conditions and the resistance to interlaminar failure of the resulting composites can be optimized by changing the consolidation temperature. In this study, the consolidation temperature has been varied from 260 up to 285 °C by steps of 5 °C. The following conclusions can be drawn:

(i) In the longitudinal direction, the bending modulus is substantially independent of the consolidation temperature with an average value of about 39 GPa, while the maximum stress in the outer layer increases from 157 MPa at $T_c = 260$ up to 259 MPa at $T_c = 285$ °C.
(ii) The transversal bending modulus and maximum stress and the interlaminar shear strength values markedly improve as the consolidation temperature increases. In particular, both the maximum transversal bending stress and ILSS values improve by a factor of 2.8 as $T_c$ varies from 260 up to 285 °C.

(iii) Up to $T_c = 280$ °C the Charpy impact resistance of the investigated composites oscillates around an average value of 79 kJ/m² and for $T_c = 285$ °C decreases to 64 kJ/m². At the same time, the ductility index presents a maximum value of 9 at $T_c = 265$ °C and then it monotonously diminishes down to a minimum value of 4.5 at $T_c = 285$ °C.

Acknowledgments

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References


