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Dynamic Mechanical and Perforation Impact Behavior of All-PP Composites Containing Beta-Nucleated Random PP Copolymer as Matrix and Stretched PP Homopolymer Tape as Reinforcement: Effect of Draw Ratio of the Tape

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ABSTRACT: Cross-ply all-polypropylene (PP) composite laminates were prepared by hot consolidation after tape winding combined with film stacking. Alpha (α) PP tapes of different draw ratios (DR = 8 and 12), produced by online extrusion...
stretching, served as reinforcements. Beta (β)-nucleated random PP copolymer, introduced in the form of a film, composed the matrix. The E-modulus of the PP tapes increased whereas their density decreased with increasing DR. The volume fraction of the reinforcement and the void content were estimated using optical microscopic images. The all-PP composites were subjected to dynamic mechanical thermal analysis, flexural, and instrumented falling weight impact tests. It was found that with increasing draw ratio of the α-PP tapes, the stiffness, strength, and perforation resistance of the composites were improved.

**KEY WORDS:** all-polypropylene composite, dynamic mechanical thermal analysis, instrumented falling weight impact, polypropylene, draw ratio.

**INTRODUCTION**

In the automotive industry, polymers have made a major inroad in the past decades to make parts such as body panels, underbody structures, dashboards, seating components, front ends, and bumpers. Polypropylene (PP) is the base material for a large number of such applications. It is cheap, can be reprocessed several times without significant loss of properties, and can be easily modified to achieve specific requirements. In order to compete with standard engineering plastics, the stiffness and strength of PP has to be improved; usually, that occurs on glass fiber reinforcement. Although both PP and glass are easy recyclable alone, recycling becomes a problematic issue when they are combined. Current trends toward environmentally-friendly composite systems focus on the use of natural fibers, like flax and hemp, as alternatives for glass fibers. Although these fibers do have some ecological advantages over glass fibers, since they are renewable, and even incinerable, natural fibers do not offer significant advantage with respect to recycling via remelting.

Self-reinforced composites represent an effective alternative to the traditional fiber-reinforced composites where the matrix and the reinforcement are from the same polymer, thereby supporting the ease of recyclability. This topic has gained interest since Capiati and Porter [1] (mid 70s) showed the benefits of ‘single polymer composite’ production on an example of polyethylene. Later on, the group of Hine and Ward [2] succeeded to convert via, ‘hot compaction,’ a part of polymer fibers into matrix in which the residual fibers were embedded. This material is nowadays commercially available as Curv® [2]. The creation of highly oriented co-extruded PP tapes allows the production of recyclable ‘all-polypropylene’ (all-PP) composites with a larger temperature processing window (20–40°C) than hot compaction. The outer surface layers of the tape, given by a PP copolymer, will form the matrix after hot consolidation. As the thickness of the surface layers can be very small, the reinforcing
content given by the oriented PP homopolymer in the midsection may be very high [3–6]. The product is available under the trade name Pure®.

The most recent development with all-PP composites is to exploit the polymorphism-related difference in the melting range of beta (β)- and alpha (α)-phases. The former works as the matrix, whereas the latter as the reinforcement. The feasibility of this concept has been shown [7,8]. Note that the β-PP has a markedly lower melting point than the alpha version [9]. Therefore, the β-PP is foreseen for the role of matrix, while the stretched α-PP should work as reinforcement. The resulting composite may be really a PP homocomposite as the matrix and the reinforcement differ from one another only in their crystalline modifications. On the other hand, in order to enlarge the difference in the melting temperatures of the matrix and reinforcing phases, the selection of a random β-PP copolymer (β-rPP) for the matrix is straightforward. Hence, the target of this project was to produce all-PP composite laminates in which the reinforcing tapes, arranged in cross-ply (CP) manner, are sandwiched in between β-rPP layers via film stacking and heat consolidated. The aim of this study is to determine the mechanical and perforation impact behavior of the corresponding all-PP composite laminates as a function of the draw ratio of the reinforcing tape.

**MATERIALS**

**Manufacture of Laminates**

The PP tapes foreseen as reinforcements of the laminates were produced in our laboratory using twin screw extruder as described elsewhere [8]. It is well known that the tensile strength and stiffness of PP tapes can be dramatically enhanced by (super)molecular orientation achieved during solid state drawing [10–14] and hence it can be used as reinforcement for a composite material. Taking this into consideration, we have constructed a stretching unit with hot air chamber in which stretching occurred and molecular orientation in the preferred direction could be obtained. The details of the stretching unit are discussed elsewhere [15]. In short, PP tape coming out from the extruder is passed through a water bath and entered into the stretching unit through the take-off roller. The temperature inside the stretching unit chamber was kept at 100°C by blowing hot air. Then, the tape was wound four times (loops) between two rollers, which is rotating inside the hot air chamber. Four windings were consistently used to ensure the tape ‘softening’ prior to its stretching. The tape was pulled out from the hot air chamber by another roller, the speed of which was computer-controlled similarly to those of the chamber. Tapes of different draw ratios (DR) were produced by increasing the speed of the take-off roller kept...
outside the hot air chamber compared to those within. DR was determined as the ratio of the cross-sectional area of the undrawn material to that of the drawn one. We have produced PP tapes with DRs of 6, 8, 10, and 12 by varying the speed of the rollers, as mentioned above. In this article, we have compared the properties of all-PP laminates fabricated using DR = 8 and DR = 12, respectively. Characteristics of the PP tapes used for the preparation of the laminates are summarized in Table 1.

Thin film of beta-polymorph rich random PP copolymer (β-rPP) [9] (Tipplen R351F of Tisza Chemical Works, Hungary; melt flow index 8.5 g/10 min at 230°C and 2.16 kg load) served as the matrix. For the β-nucleation of the PP, first a masterbatch was produced in a Brabender extruder with 1.5 wt% of calcium salt of suberic acid that was introduced as a selective β-nucleating agent. In this study, β-nucleated films with a thickness of 180 μm were extruded by in-situ mixing the neat rPP with the masterbatch, resulting finally in a β-rPP with 0.15 wt% nucleator content. To promote the β-crystallization of the PP, the take-up rolls were heated close to 100°C, because the preferred crystallization temperature range of the β-modification of PP is between 100°C and 140°C [16].

Details of the fabrication of the all-PP composite laminates are described elsewhere [5,17,18a,18b]. In short, the manufacture of the PP laminates involved a two-stage process: winding of the PP tapes ((0°/90°)(CP)), and consolidation of the related tape containing fabric using hot pressing. Before winding the PP tapes, a thin β-rPP film layer was placed on the surface of a thin steel plate. Using a winding machine, supplied by Bolenz & Schaefer Maschinenfabrik (Biedenkopf, Germany), PP tapes were wound from a bobbin onto the same steel plate rotating at a constant speed. After laying one layer of PP tape, another layer of β-PP film was placed and the winding direction on the steel plate was changed for CP lay-up. The same process continued and the total numbers of layers of PP tapes and β-PP film were kept 10 and 11, respectively. A similar winding process was already adopted for manufacturing all-PP composites from coextruded Pure® tapes [19].

**Table 1. Characteristics of alpha PP tapes.**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>DR = 8</th>
<th>DR = 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
<td>1.25 mm</td>
<td>1.1 mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>100 μm</td>
<td>100 μm</td>
</tr>
<tr>
<td>Density</td>
<td>0.862 g/cm³</td>
<td>0.853 g/cm³</td>
</tr>
<tr>
<td>Composition</td>
<td>Homopolymer</td>
<td>Homopolymer</td>
</tr>
<tr>
<td>Heat of fusion (J/g)</td>
<td>101.4 ± 0.4 J/g</td>
<td>103.9 ± 0.4 J/g</td>
</tr>
<tr>
<td>Tensile modulus (ISO 527)</td>
<td>6.4 ± 2 GPa</td>
<td>8.5 ± 1.5 GPa</td>
</tr>
</tbody>
</table>

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All-PP composite laminates were produced by hot pressing in a laboratory press (P/O/Weber GmbH, Remshalden, Germany) at a temperature of 145°C with a fixed holding time of 8 min under a pressure of 7 MPa. All-PP composites made out of PP tape with DRs 8 and 12 are denoted as all-PP/DR8 and all-PP/DR12, respectively, in the following sections of this article.

EXPERIMENTAL

Differential Scanning Calorimetry

For the thermal characterization of reinforcing PP tapes and all-PP composite laminates, differential scanning calorimetry (DSC) was used. DSC traces were recorded using Mettler-Toledo DSC821 instrument (Greifensee, Switzerland). In order to demonstrate the occurrence of α and β modifications, the first heating scan ($T = 25–200^\circ\text{C}$) was followed by a cooling one to $T = 100^\circ\text{C}$, prior to a second heating cycle to $T = 200^\circ\text{C}$. The temperature corresponding to the peak of the endotherm was considered as the melting temperature, $T_m$. This heating/cooling program was selected based on the recommendation of Varga [9].

Density Measurement

Density measurements were done at room temperature (23°C ± 1°C) in a highly sensitive balance (DV 214C) for measuring density provided by the company Ohaus (Naenikon, Switzerland). The liquid used for measuring the density of the sample was heptane. The average value from five specimens was taken for each measurement.

Optical Microscopy

Microscopic images of the cross-section of the all-PP laminates were captured by a stereomicroscope (Leitz, Germany) equipped with a high-resolution digital camera. The IMAGE-C analysis software was used to estimate the void content from the micrographs.

Dynamic Mechanical Thermal Analysis of All-PP Composites

Dynamic mechanical thermal analysis (DMTA) of all-PP composite laminates was performed in dual cantilever flexural mode. Specimen were cut from the composite plates with dimensions of 60 mm × 15 mm × 2 mm (length × width × thickness) and measured in a DMTA Q800
(TA Instruments, New Castle, USA) machine equipped with a data acquisition software. The specimens were cooled to −50°C. The temperature was allowed to stabilize and then increased in a stepwise manner by 3°C, kept 5 min isothermal at each step, until 120°C. The specimen was subjected to a sinusoidal flexural displacement applying a maximum tensile strain of 0.1% (which was well within the viscoelastic region) at a constant frequency of 1 Hz.

**Static Flexural Test**

The static flexural properties of the all-PP composites, such as modulus of elasticity, ultimate flexural strength, and strain at elongation were determined following the DIN EN ISO 178 standard on a Zwick 1445 (Ulm, Germany) test machine. A support span of 32.8 mm was used in the three-point bending setup. A cross-head speed of 1 mm/min was applied during the test and the elastic modulus was calculated in the strain range 0.05–0.25%. Load was applied using a U2A type 10 kN load cell. A preload of 5 N was applied in the beginning of each test and the mean value of five specimens tested was reported for each type of laminates.

**Instrumented Falling Dart Impact**

Instrumented falling weight impact (IFWI) tests were performed on a Fractovis 6785 (Ceast, Pianezza, Italy) using the following settings: incident impact energy, 229.05 J; diameter of the dart, 20 mm; diameter of the support rig, 40 mm; weight of the dart, 23.357 kg; drop height, 1 m. IFWI tests were performed on quadratic specimens of 60 mm × 60 mm at room temperature.

**RESULTS AND DISCUSSION**

Characteristics of the α-PP tapes at different DRs are given in Table 1. The drawing resulted in a high degree of molecular orientation associated with more than 37% enhancement in stiffness as the DR increased from 8 to 12. A higher enthalpy of fusion with increasing DR is also observed, which indicates the increase in crystallinity of the tape. The DSC traces of β-rPP film and all-PP/DR12 are shown in Figure 1. The melting temperature of the reinforcing PP tape ($T_m \approx 163°C$) is higher than that of the β-PP matrix ($T_m \approx 131°C$) used in this study. There is an additional peak at 155°C observed in the case of the all-PP laminate which is not present in the DSC trace of either α-PP tape or β-rPP. This is due to the partial transformation
of $\beta$ to the $\alpha$ modification occurring via a melt recrystallization process [20,21].

Parameters on the consolidation quality of all-PP laminates with $\alpha$-PP tapes of different DRs are given in Table 2. The corresponding data show that the density of all-PP laminates is higher than that of the initial PP tapes. This can be explained by the fact that the microvoids in the PP tapes have been ‘healed’ during hot consolidation. Light microscopic photographs in Figure 2 show the characteristic cross-sections of the all-PP laminates produced. Using the IMAGE-C analysis software, the void contents in all-PP laminates with tapes DR = 8 and DR = 12 were found to be 4 and 2.8 vol.%, respectively. This implies that a slightly better consolidation of the laminates could be achieved by increasing DR of the reinforcing $\alpha$-PP tapes, which in turn led to improved mechanical properties which is discussed in the following part of this article. It is well known that the reinforcement–matrix interface must have appropriate chemical and physical features to provide the necessary load transfer from the matrix to the reinforcement [22]. We have previously reported that the transcrystallization phenomenon is responsible for the transfer of stress from the ‘weak’ $\beta$-rPP matrix to the ‘strong’ $\alpha$-PP reinforcement [15].

The dynamic mechanical behaviors of all-PP composite laminates with tapes of DR = 8 and DR = 12 are shown in Figure 3. At room temperature, the all-PP composite laminates containing tapes of DR = 8 and DR = 12
possess storage moduli \((E')\) of 2.25 and 3.7 GPa, respectively. The loss factor, \(\tan \delta = E''(\text{loss moduli})/E'(\text{storage moduli})\) as a function of temperature for the all-PP composite laminates is also shown in Figure 3. The \(\tan \delta\) peaks represent different relaxation transitions. The related traces show a \(\tan \delta\) peak near 0°C which corresponds to the \(\beta\)-relaxation \((T_g)\) of PP in all-PP laminates. A more definite \(\tan \delta\) peak, corresponding to the \(\alpha\) transition \((T_\alpha)\), appears at approximately 90°C in Figure 3. The position of \(T_g\) remained nearly unchanged, but its peak intensity decreased significantly with increasing DR of the reinforcing tape. At high stretching, the amorphous phase becomes highly oriented between the crystalline regions and it has less freedom to be involved in segmental motions. The higher the stiffness of the tape, the lower the magnitude of the corresponding \(T_g\) is. This can also be observed for the composites containing \(\alpha\)-PP tapes with increasing DR.
Parallel to the dynamic flexural tests, short-term static flexural tests were also conducted. Figure 4 shows a plot of the experimental results obtained in the flexural test of the all-PP composites. These results show that flexural strength and modulus of the all-PP laminates are markedly improved by incorporating reinforcing PP tapes with increasing DR. This enhancement is partly due to the reduction in the void content of the all-PP laminates having PP tapes with DR = 12 (cf. Table 2). The failure mode of the specimens was typical to that of ductile materials. The specimen started yielding after reaching a maximal stress. Typical flexural stress–strain diagrams for the all-PP laminates are shown in Figure 4.

The falling dart impact strength was evaluated from the IFWI tests performed at room temperature. The results indicate that the specific (i.e., thickness-related) perforation impact energy is enhanced with increasing DR of the reinforcing PP tape. The fiber–matrix interface is the critical factor that determines to what extent the potential of the reinforcing phase in the composites can be exploited and maintained during use. The basic idea with self-reinforced composites is that interfacial bonding should be improved if matrix and reinforcement are made from the

![Figure 4. Flexural properties of all-PP laminates at room temperature: (a) typical flexural stress–strain curve and (b) flexural strength and flexural modulus of the all-PP laminates. Note: The testing is done at room temperature.](image)

Table 2. Characteristics of the all-PP composite laminates (tape arrangement: CP).

<table>
<thead>
<tr>
<th></th>
<th>$\beta$-rPP-8(all PP composite)</th>
<th>$\beta$-rPP-12(all PP composite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.905 ± 0.001</td>
<td>0.902 ± 0.004</td>
</tr>
<tr>
<td>Void content (%)</td>
<td>4.0 ± 0.2</td>
<td>2.8 ± 0.5</td>
</tr>
<tr>
<td>Reinforcement (%)</td>
<td>51.86 ± 0.876</td>
<td>52.5 ± 0.876</td>
</tr>
</tbody>
</table>

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same semi-crystalline polymer. From force vs. time plots obtained from the laminates, it can be easily recognized that the all-PP/DR12 is more damage tolerant (Figure 5). The photographs of typical failure behavior of the laminates after the falling dart impact tests are shown in Figure 6. We can see simple penetration, delamination with fibrillation, and no penetration of the dart through the specimen with same dimensions, in the case of β-PP matrix, all-PP/DR-8, and all-PP/DR-12, respectively. When the consolidation is poor, the failure occurs typically by delamination and tape pullout [17]. With increasing consolidation quality, the delamination becomes less pronounced when the specimens break. In this case, for the laminates of these dimensions, the falling dart was seen to rebound following impact with all-PP/DR-12 (as indicated by arrow in the Force vs time graph). This specimen had better consolidation and the specimen was able to move sideways during impact, allowing the dart to pass through the opening of the specimen holder. Therefore, the Force vs. time curve appears to be same for

![Figure 5](image_url1). Representative force vs time curves: (a) All-PP/DR8 laminate and (b) All-PP/DR12 laminate. Note: Arrow indicates the rebounding of the dart.

![Figure 6](image_url2). Typical perforation failure of the specimens of all-PP laminates after IFWI of: (a) β-PP matrix (no fractogram is given), (b) all-PP/DR8, and (c) all-PP/DR12. Note: All tests were done at room temperature.
both laminates, but, actually, all-PP/DR-12 is not broken and we cannot calculate the energy absorption ability (perforation energy). These results clearly indicate that the mechanical properties of the laminate can be tuned by varying the draw ratio of the reinforcement for a specific application. Barany et al. [17,18] reported earlier in the related field that the tensile and flexural properties are found to increase, whereas the perforation energy decreases with the consolidation degree for all-PP composite laminates.

**CONCLUSION**

All-PP composites with CP architecture were successfully produced from α-PP tapes (reinforcement) and β-rPP film (matrix) by a hot consolidation method. The DRs of the tapes in the CP laminates were varied. The properties of the all-PP composites were determined in DMTA, static flexural, and IFWI tests. It was established that the DR of the reinforcing tape has a strong influence on the static and dynamic mechanical properties of the composite laminates. With increasing DR of the α-PP tapes, both the stiffness and strength data were improved. This enhancement was attributed to the higher stiffness and strength of the reinforcement, and partly also to a better consolidation degree achieved. The IFWI results showed that the resistance to dart penetration is higher at the higher DR values of the reinforcing α-PP.

**REFERENCES**


