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Processing of Multilayered Filament Composites by Melt Blown Spinning

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ABSTRACT: Newly designed layer multiplying blocks are introduced in the process line of a melt blown spinning machine. The layer multiplying blocks have the capability to produce filament composites up to 1025 layers. Multilayer filament composites of polypropylene (PP) with poly(caprolactone) (PCL), a water soluble polyester or poly(L-lactic acid) are successfully produced in the form of nonwovens. Selected samples of PP/PCL are delaminated using the following methods: semi-crystalline PP/PCL samples are soaked in chloroform and agitated, and amorphous PP/PCL samples are subjected to mechanical stress in the axial spinning direction. Results show the possibility to create thin ribbons with extremely high surface area. The produced nonwovens and ribbons are characterized by field emission scanning electron microscopy and by differential scanning calorimetry. The extremely high surface area ribbons can be applied in different fields where high surface area is required, such as filtration, energy applications, catalysis, or tissue engineering.
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INTRODUCTION

Melt blown spinning is a common and rapid process for production of nonwoven fiber mats.[1,2] The melt blowing process involves using one or more jets of hot gas, usually air, to attenuate molten polymer streams into fine filaments.[3,4] The produced fibers' dimensions lie in between 0.1 and 100 μm.[5] From an industrial point of view, melt blown spinning offers many desirable advantages over other spinning techniques such as electrospinning, melt spinning, dry spinning, etc. First, the simplicity of this technique allows fibers to be produced from the polymer melt in one step.[6] The melt is directed by extruders to an orifice die and is stretched into fibers by aerodynamic force. Second, the scalability of this technique allows it to be used on an industrial scale for large production of nonwovens.[7] The melt blown spinning technique has already been transitioned to industrial scale with production rate capabilities of up to 1500 g min^{-1}.[8] The third advantage is related to the environmental point of view: as the fibers are produced from the molten polymer, the use of non-recoverable toxic solvents can be avoided.[8]

In a typical melt blown spinning process, as depicted in Figure 1, a thermoplastic polymer resin is stored in a hopper and delivered by extruder shaft or screw to the die.[9] As the polymer is transported to the die, it heats up and melts at a specific temperature appropriate for fiber processing.[10] At the die face, the polymer melt is delivered at the spinneret and stretched by two hot compressed air jet streams supplied from a V-shape slot.[11,12] The drag forces resulting from the air jet will convert the polymer melt into fibers deposited on the target.[12,13]

The history of the melt blown process goes back to 1950, when a naval research laboratory first demonstrated the melt blown process line for production of fine deiner fibers.[14] The process was used for production of microfilters used for collection of radioactive particles in the upper atmosphere.[14] In the mid 1960s, Exxon recognized the significance of the melt-blown

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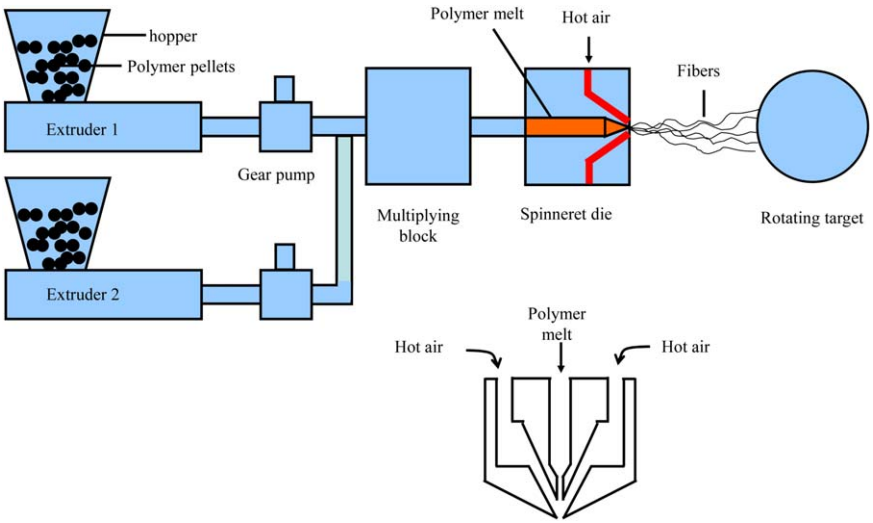

Figure 1. Schematic illustration shows the components of melt blown spinning machine. The lower illustration shows the design of the spinneret die. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

process, also they sought end uses for their commercialized polyolefins such as polypropylene (PP) and polyethylene.[15] After 5 years, a prototype model for the production of microfibers was successfully patented.[15] Within the last 20 years many activities have been done outside Exxon facilities at companies such as at 3M. 3M has developed many processes for production of blended microfibers with textile deiner fibers.[15]

For this article, a newly designed layer multiplying block was introduced as an extra part of melt blown process line, incorporated between the gear pump and spinneret, as shown in Figure 2. The multiplying block, shown in Figure 2, creates multilayer filament composites. The composite consists of two different kinds of polymers. Depending on the number of multiplying blocks used a filament with three layers (without any multiplying blocks) and up to 1025 layers (with nine multiplying blocks) can be manufactured. The initial three-layer filament is formed as follows: two polymer melt streams come from two extruders, one of these streams is divided into two substreams, which fuses together with the undivided stream to form one three-layer filament. At the first multiplying block, the main melt stream will be divided into right and left substreams as shown in Figure 2. The right substream will go down and the left substream will go up. The two divided substreams meet again after passing through the multiplying block. This will result in five layers filament. By consequent multiplication and fusing of the main stream, the filament produced after nine multiplying block passes will consist theoretically of 1025 layers. The resulting number of layers can be expressed by eq. (1):

$$L_n = 2^{n+1} + 1 \quad (1)$$

where L_n is the number of layers produced and n is the number of multiplying blocks.

To the best of our knowledge, multilayered films consists of 201 alternative poly(styrene) and poly(methyl methacrylate) have been produced by co-extrusion.[16,17] The authors did studies on the optical and mechanical properties of the produced films. The work does not include the extrusion of multilayered fibers with wide variety of polymers.[16,17]

EXPERIMENTAL

Materials

PP (MF 650 W) with melt flow index (MFI) 500 g 10 min^{-1} at 210°C is purchased from 3M (St. Paul, MN), PP (PP 3155) with MFI 36 g 10 min^{-1} and elastomeric PP (VM 2330) with MFI 300 g 10 min^{-1} are purchased from Exxon Mobile Chemical Company (Huston, TX), poly(caprolactone) (PCL) 6250 with MFI 9 g 10 min^{-1} at 80°C is purchased from Porstorp winning formula (Warrington, UK), water soluble polyester (Eastman AG ^{TM} 38S polymer) is purchased from Eastman Chemical Company (Kingsport, TN), and polylactide of MFI 80 g 10 min^{-1} at 210°C (Ingeo^{TM} Biopolymer 3251D) is purchased from Jamplast Inc. (Ellisville, MO). All materials are used as received except the water soluble polyester which is dried at room temperature (23°C) in a vacuum oven overnight prior to use. For spinning multilayer composite filaments, the following combinations are used: PP 650 W/PCL 5260, VM 2330/PCL 6250, PP 3155/water soluble polyester and PP 3155/polylactic acid. These combinations have been chosen according to the

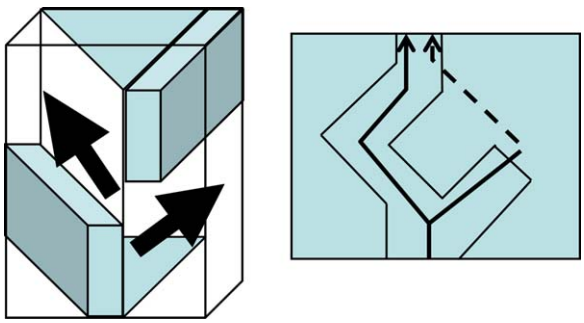

Figure 2. Schematic illustration shows the design of a multiplying block, left: Front view, right: Top view. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Different Polymer Combinations and Their Melting Temperature and Delamination Method

Sample	Polymer 1	Polymer 2	No. of multiplying blocks	Processing temperature (°C)	Collector die distance (cm)	Delamination method
S1	PP 650 W	PCL Capa 6250	0	180	23	CH_3Cl
S2	PP 650 W	PCL Capa 6250	4	180	23	CH_3Cl
S3	PP 650 W	PCL Capa 6250	6	180	23	CH_3Cl
S4	PP 650 W	PCL Capa 6250	7	180	23	CH_3Cl
S5	PP 650 W	PCL Capa 6250	8	180	23	CH_3Cl
S6	PP 650 W	PCL Capa 6250	9	180	23	CH_3Cl
S7	VM 2330	PCL Capa 6250	0	200	36	Mechanical
S8	VM 2330	PCL Capa 6250	4	200	36	Mechanical
S9	VM 2330	PCL Capa 6250	6	200	36	Mechanical
S10	VM 2330	PCL Capa 6250	7	200	36	Mechanical
S11	VM 2330	PCL Capa 6250	8	200	36	Mechanical
S12	VM 2330	PCL Capa 6250	9	200	36	Mechanical
S13	PP 3155	water soluble polyester	0	240	31	N/A
S14	PP 3155	PLA	0	240	25	N/A

similarity of the melt processing temperatures, as well as different ribbon delamination mechanisms.

Melt Blown Spinning

The polymers are fed into the two hoppers and then melted and extruded to the spinneret. The total rotation speed of the two gear pumps is set at 30 rpm and the rotation speed ratio between gear pump 1 and gear pump 2 is kept at 1 : 1. The screw speeds of the extruders 1 and 2 are adjusted automatically by the melt blown spinning machine to build up an input pressure inside the extruders of 160 psi. Therefore, depending on the melt flow index of the used polymer the screw speed are ranged between 8 and 20 rpm. The melt temperature and the spinneret-to-target distance are set for each combination, as shown in Table I. These parameters are chosen in order to get homogeneous, non-sticky fiber mats. The melt blown samples are collected on a rotating cylindrical metallic target with an 8 cm diameter. Samples are collected at a rate of 10 rpm.

Delamination Process

After sampling of the nonwovens, the best quality samples, which show almost no micro- and macro-defects under field emission scanning electron microscopy (FE-SEM), are chosen for the delamination process. Delamination is taken place either by soaking the fleece in a good solvent for one component of the filament or by applying longitudinal mechanical load in the axial spinning direction. For the first delamination method, 5 cm × 1 cm rectangular nonwoven samples are soaked in a solvent and sonicated for 30–90 min. For the mechanical delamination method, rectangle samples of size 5 cm × 10 cm are fixed by the grips of Instron 5848 Microtester device. The displacement rate of the grips is fixed at 1 mm min^{-1}. The sample is elongated until fracture. Table I shows the suitable delamination methods used for each composite combination.

Characterization

The spun composite filaments are characterized before and after delamination by FE-SEM (Zeiss) to observe the structure and the thickness of delaminated layers.

Additionally, the tensile tests are performed to examine the changes in strength before and after delamination. A sample of 10 cm × 1 cm is placed between the grips of the tensile stress tester (Instron 5848 Microtester) and is stretched with the test speed of 1 cm min^{-1}. The obtained values are the average of five individual tests for each sample.

The differential scanning calorimetry (DSC) measurements were conducted on a TA Instruments Q2000 modulated differential scanning calorimeter equipped with an RCA90 refrigerated cooling accessory. The sample weights ranged from 5.3 to 7.0 mg. The samples were encapsulated in standard aluminum pans. The samples were cooled to 10°C and heated at 5°C min^{-1} to 90°C under a 50 mL min^{-1} nitrogen purge. The heat of fusion was determined by integrating the melting endotherm from 40°C to 70°C.

RESULTS AND DISCUSSION

Sample Quality

The samples in Table I are spun at the mentioned melt processing temperatures and the spinning condition mentioned in the experimental section. It is observed that the combinations of PP 650 W/PCL 6250 and VM 2330/PCL 6250 produced the best quality samples as can be seen in Figure 3(A,B), respectively. Fibers produced from other combinations, including PP 3155/water soluble polyester and PP 3155/PLA contained many fibrous defects, as shown in Figure 3(C,D), respectively.

Delamination Method

Delamination by Solvent. The chosen nonwoven samples (S1–S12) are soaked in chloroform and agitated in an ultrasonic bath for different time intervals (30–90 min). The samples are

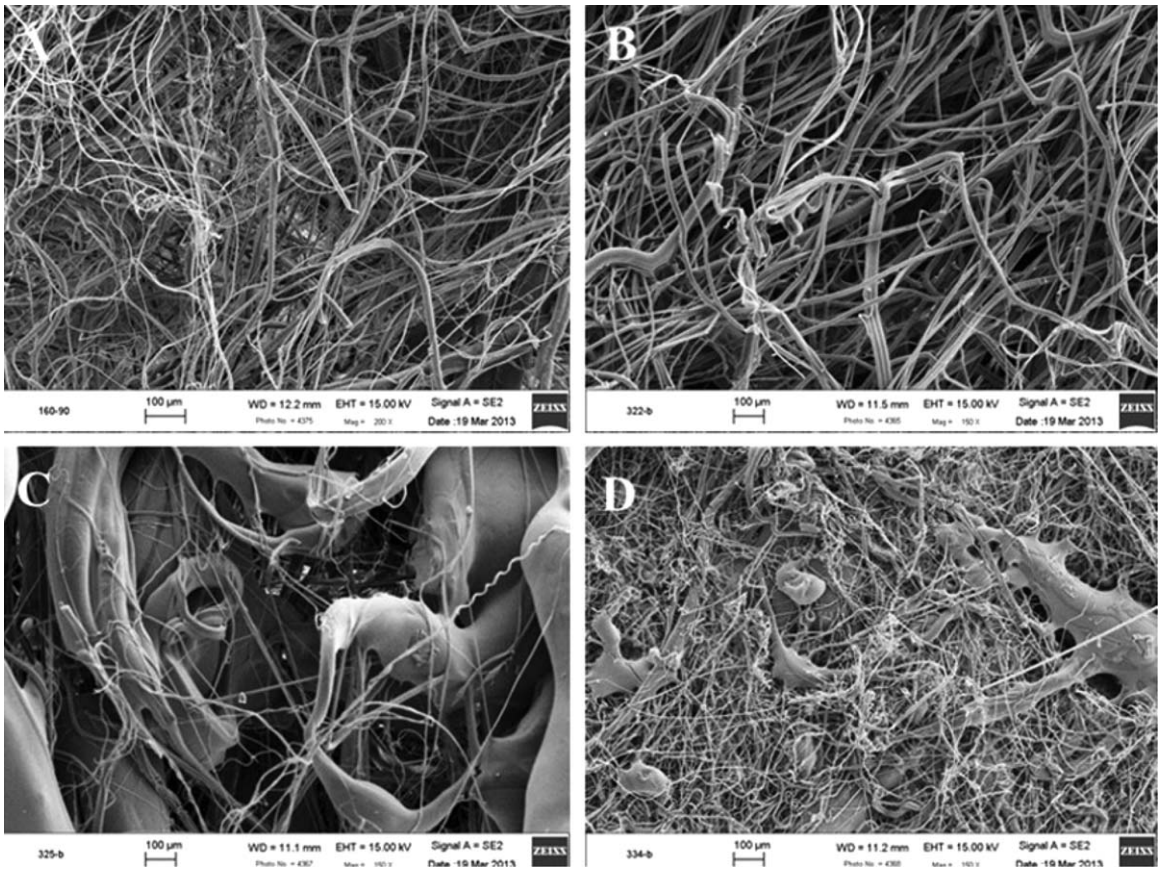

Figure 3. Melt blown spun fibers from different polymer combinations spun from four multiplying blocks: (A) PP 650 W/PCL 6250, (B) VM 2330/PCL 6250, (C) PP 3155/water soluble polyester, and (D) PP 3155/PLA.

then dried at room temperature overnight prior to characterization. Results show that delamination occurred with fibers of PP 650 W/PCL as the PCL is dissolved. On the other hand, the soaked fibers of VM 2330/PCL fused together, as can be seen in Figure 4. VM 2330 lacks crystals because it is amorphous PP; therefore, solvent molecules can penetrate in between the polymer chains and swell them resulting in the formation of fused fibers.

In order to optimize the delamination method, samples of PP 650 W/PCL 6250 are sonicated at different time intervals ranging from 30 to 90 min. Figure 5 shows that the higher the sonication time, the better the delamination process occurred. At higher number of layer multiplying blocks, more layers are delaminated. It is impossible to see aligned arrays of ribbons after delamination as the resulted ribbons are rolled up or collapsed after removing the intermediate layers of PCL 6250;

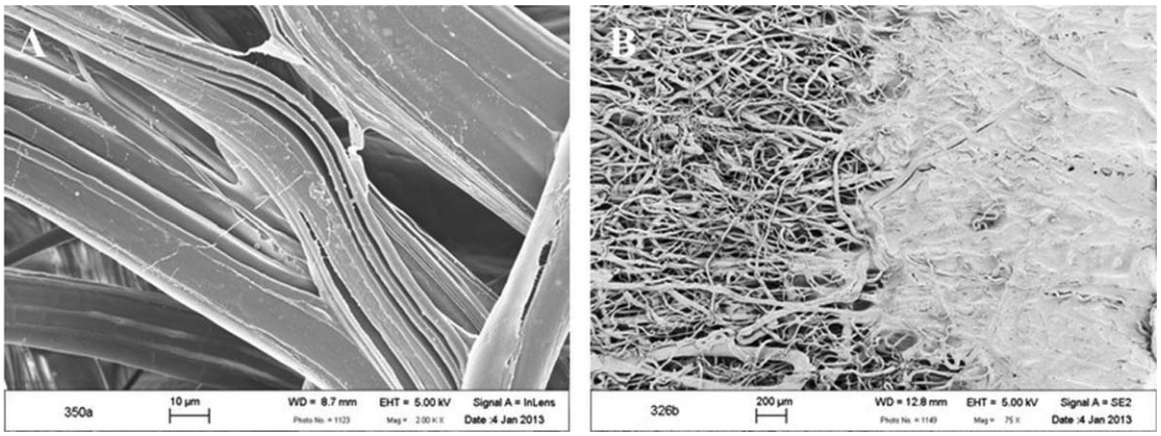

Figure 4. SEM micrographs of delaminated and fused multilayer composite filaments: (A) PP 650 W/PCL 6250 and (B) VM 2330/PCL 6250.

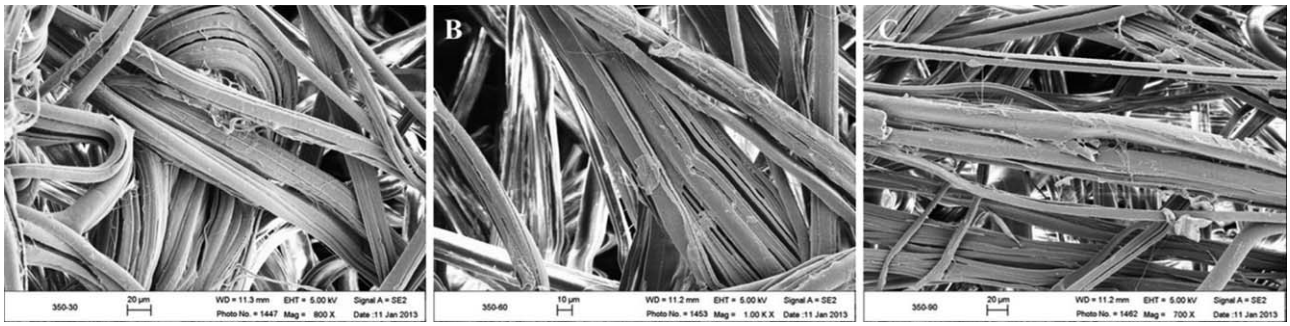

Figure 5. SEM micrographs show the efficiency of delamination process for sample S4 (seven multiplying blocks, 257 layers) at different time intervals: (A) 30 min, (B) 60 min, and (C) 90 min.

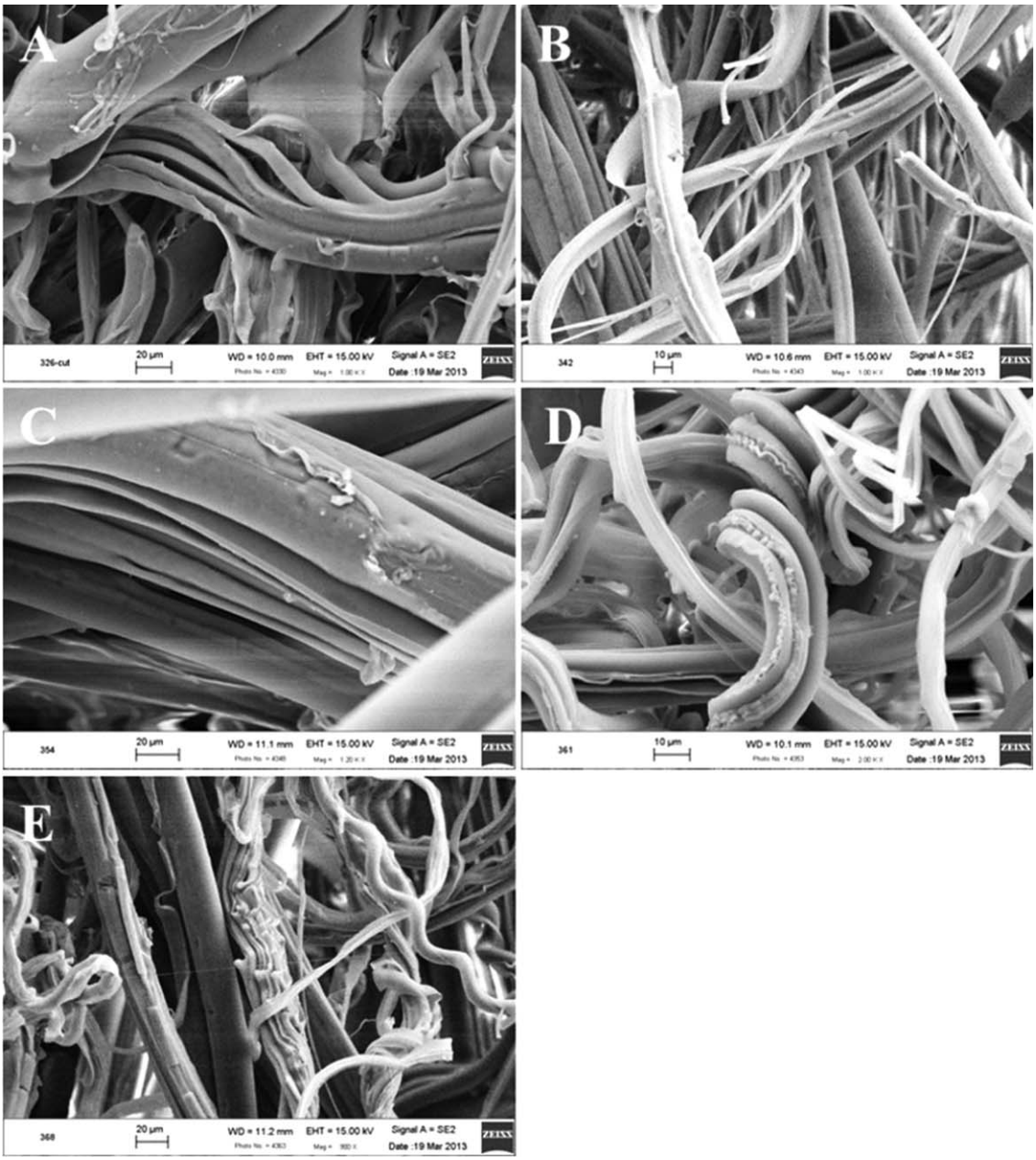

Figure 6. SEM graphs show delaminated VM/PCL 6250 fibers by mechanical stress: (A) Sample S8, four multiplying blocks (33 layers), (B) Sample S9, six multiplying blocks (129 layers), (C) Sample S10, seven multiplying blocks (257 layers), (D) Sample S11, eight multiplying blocks (513 layers), and (E) Sample S12, nine multiplying blocks (1025 layers).

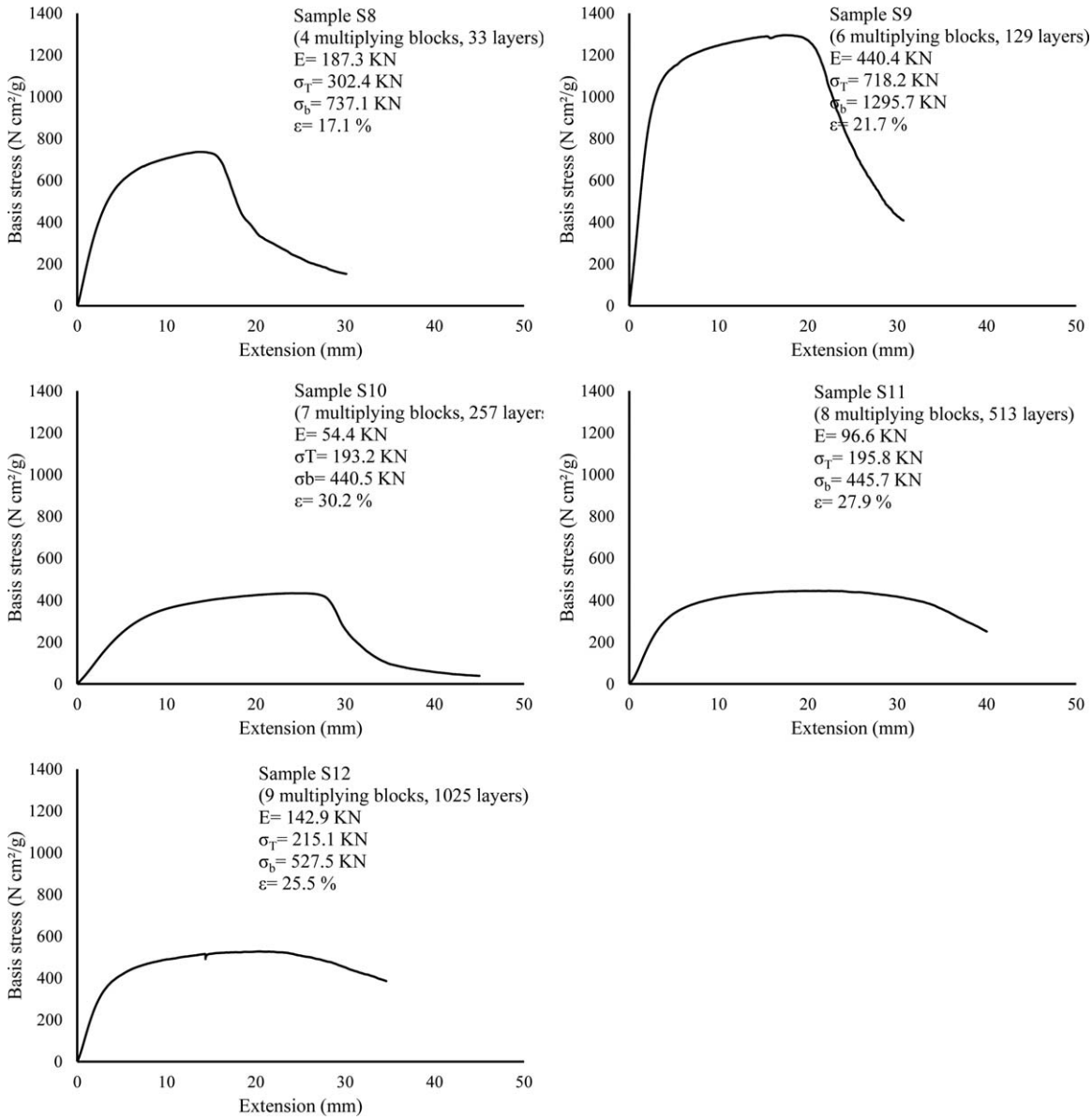

Figure 7. Extension-basis stress curves for mechanically delaminated fibers.

however, the mean average thicknesses of ribbons can give us an indication about the supposed number of layers. Theoretically, if it is supposed that the average mean fiber diameter ranged from 15 to 20 μm based on fiber diameter measurements from Figure 3(A,B), the ribbon thickness will be reduced to about 5–7 μm (at 0 layer multiplying blocks) down to 14–20 nm (at nine layer multiplying blocks).

Delamination by Mechanical Load. Samples of VM 2330/PCL 6250 are chosen for delamination via the application of axial stress along the spinning direction. During mechanical delamination, a stress at the contact surface between PCL and VM 2330 ribbons is created. The mechanical stretch causes stretching of PCL and VM 2330 chains in the load direction. As PCL is semi-crystalline, the mechanical load will induce the crystallization of polymer chains parallel to each other, while the VM 2330 chains will not crystallize. After removing of the mechanical stress, the VM 2330 will relax faster than the chains of PCL. Because of the difference in elasticity between VM 2330 and PCL 6250, stress is created in the contact area between layers resulting in delamination of ribbons. SEM micrographs demonstrated in Figure 6 show the possibility for ribbon delamination by applying of mechanical stress. The ripple pattern appeared in Figure 6(D) confirms the stresses formed at the contact points between VM 2330 and PCL 6250. The advantages of the mechanical delamination method are that the layers can be delaminated without losing any of the filament's components, no organic solvent is required and a delamination step can be added to the processing line.

Mechanical properties of the delaminated nonwovens were tested. There does not appear to be a correlation between the number of layers and the mechanical properties of the samples. This could be due to having non-homogeneous thicknesses of

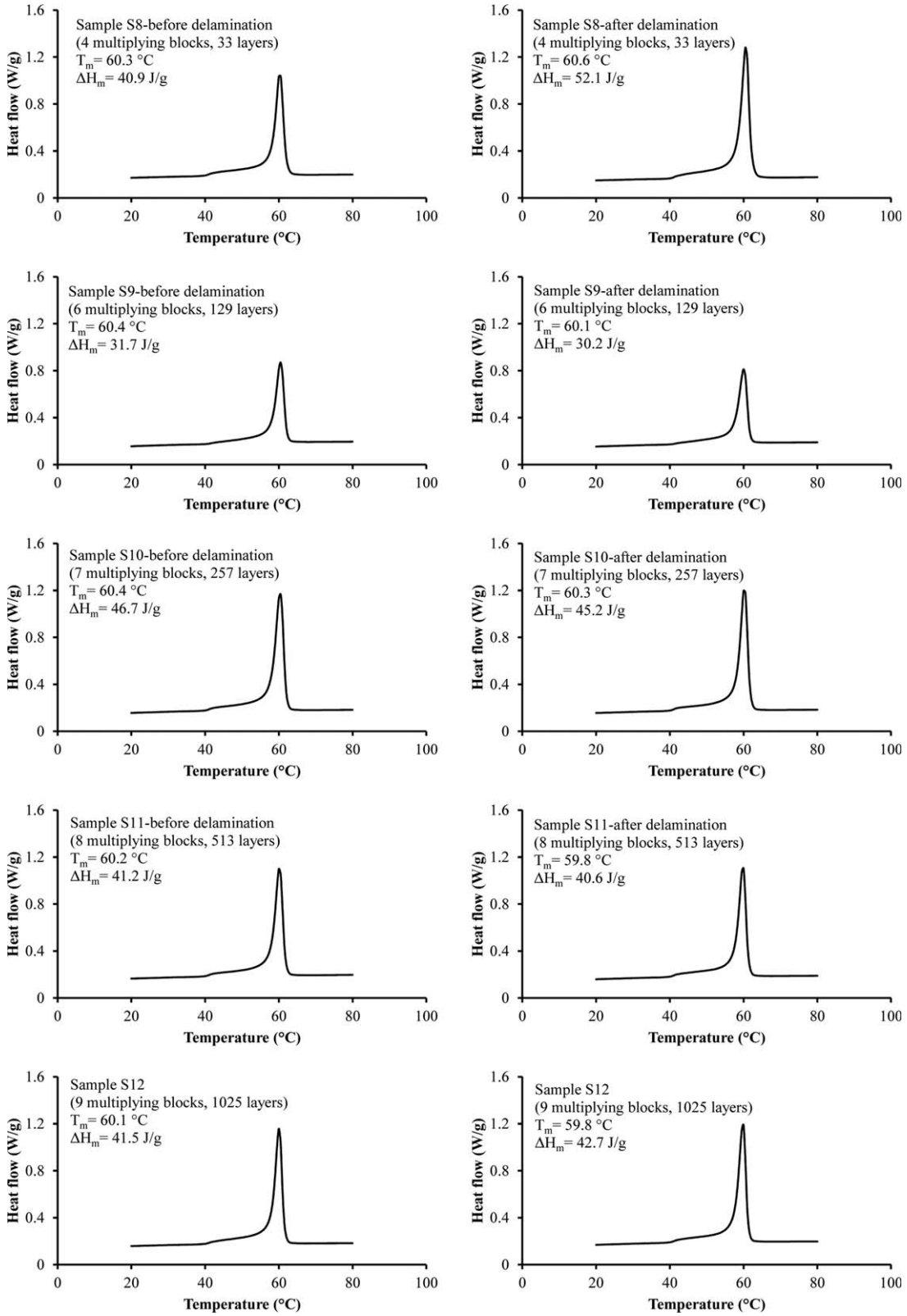

Figure 8. DSC measurements of the fibers before and after delamination at different number of multiplying blocks.

the fleeces, which influences the shape of load stress tensile curves. The basis stress versus elongation curves for the delaminated fibers with different numbers of layers are given in Figure 7. The basis stress was measured by dividing the applied force by the basic weight of the sample. The elastic moduli of the samples range from 54.5 to 440.4 kN, tensile strength ranges from 193.2 to

718.2 kN, strength at break ranges from 440.5 to 1295.7 kN, and the elongation to break ranges from 17.1% to 30.2%.

DSC results in Figure 8 show that it is possible to introduce stress induced crystallization in the PCL ribbons during mechanical delamination for filaments with 33 layers. The degree of crystallization (ΔH) for the sample S8 is increased by 27.4% from $\Delta H = 40$ J g^{-1} to $\Delta H = 52$ J g^{-1}. For samples S9–S12 no significant differences in the degree of crystallization is observed. This result corresponds to the splitting of ribbons, as shown in Figure 6, the ribbons of sample S8 were completely delaminated while the ribbons of samples S9–S12 were not fully delaminated. The difference in the degree of crystallinity in sample S8 is due to the thickness of the delaminanted PCL/PP ribbons that allows the polymer chains to be moved and oriented, while in the case of samples S9–S12, the ribbons are thin in diameter, so the chains have less opportunity to be aligned.

CONCLUSIONS

In this article, multilayer filament composites up to 1025 layers have been successfully processed by melt blown spinning. The combination of PP and PCL showed to be the best combination to obtain filaments with fewer defects than for combinations of PP with water soluble polyester or PLA. Results show that delamination of the spun filaments into ribbons is possible by soaking them in a suitable solvent for one of the components or by applying a mechanical load in the spinning direction. Ribbons of semi-crystalline PP have been created by dissolving the PCL component in chloroform, while ribbons of elastomeric (amorphous) PP and PCL have been created by applying a mechanical load. Mechanical tests show only that there is a possibility of delaminating filaments into ribbons, but it did not lead to a clear relationship between the number of formed layers and the strength of the mats. DSC results show stress induced crystallization is possible with filaments containing 33 layers, while the degree of crystallization does not increase with filaments of higher layer number. The obtained results are useful for applications where high surface area is required, as in nanoagriculture, nanomedicine, and filtration.

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