

Thermal Oxidative Degradation of Bicomponent PP/PET Fiber During Thermal Bonding Process

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ABSTRACT: The effects of the thermal bonding temperature, dwell time, and the type of mold materials on the thermal oxidative degradation of the PP sheath of bicomponent fibers were investigated using the Fourier Transform Infrared Spectra (FTIR) and Thermal Gravimetry/Differential Scanning Calorimetry (TG-DSC) techniques. The samples were prepared on a new 3D nonwovens process based on air-laying and through-air thermal bonding. The fiber material was a commercial polypropylene (PP)/polyester (PET) (sheath/core) bicomponent staple fiber. The results reveal that ketone developed following β -scission in the thermally

bonded nonwovens. The level of thermal oxidative degradation increases with increase in the bonding temperature, dwell time, and the thermal conductivity of the mold material. Such thermal oxidative degradation led to the slight widening of the melting peaks of the fiber PP sheath in the thermally bonded nonwovens, and a slight decreasing of melting point compared with those of the as-received fiber. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 391–397, 2007

Key words: fibers; processing; degradation; 3D nonwovens; thermal bonding

INTRODUCTION

Nonwoven fabrics are usually made directly from raw fiber materials in a continuous production line, thus partially or completely eliminating conventional textile operations, such as carding, roving, spinning, weaving, or knitting.^{1,2} The simplicity of fabric formation, coupled with high productivity, allows nonwovens to compete favorably with wovens and knits on a performance per cost basis in many industrial applications, from simple low cost replacements for more expensive textiles to high quality textiles. They also offer many functions that can not be filled by traditional textiles.^{1–4}

Through-air bonding is an established thermal bonding technology in the nonwoven industry. It offers process versatility, high product uniformity and loft, and a clean production process. Through-air bonded nonwovens tend to be bulky, open, soft, strong, extensible, breathable, and absorbent as well as have lower weights. It is the only thermal bonding process that allows the entire product to be exposed to a uniform temperature.^{3,4} Also, through-air bonded nonwovens can be processed without chemical binders, offering a much safer production process and working environment for machinery operators and

plant employees. Furthermore, manufacturers are able to save energy and achieve lower operating costs, as no binder preparation station is required.⁴

Recently, a new process to form 3D nonwoven fabrics, using the air laid web formation process and through-air bonding technique, has been developed in The University of Manchester.^{3–7} In this process, the fabrics were directly produced from staple fibers. The nonwoven filter samples prepared using this process are comparable and even superior to commercially available nonwoven filters in terms of microstructure, pore size distribution, air permeability and fabric area density.^{6,7} The 3D products are also even and strong. Due to the thermal bonding process, thermal plastic fibers are required. Polypropylene or polyester fibers are commonly used. Polypropylene (PP)/polyester (PET) (sheath/core) bicomponent staple fiber provides an even better raw material as it offers a greater temperature tolerance during bonding.

However, PP, like other hydrocarbon polymers, is highly susceptible to attack by molecular oxygen.^{8–13} Correspondingly, the autooxidation process, the oxidation which starts slowly but its rate increases gradually in a catalytic manner, is the major cause of irreversible deterioration leading to loss of useful properties and ultimate mechanical failure of the artifacts fabricated from these polymers. For the hydrocarbon polymers, their inherent resistance to oxidation is influenced by their chemical structures and physical and/or morphological characteristics. Increasing chain branching generally leads to more rapid autooxidation. PP containing quite a number of branching

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TABLE I
Properties of the As-Received PP/PET fiber

Linear density (dtex)	1.9
Fiber length (mm)	51
Breaking load (gf)	9.5
Breaking elongation (%)	40
Breaking tenacity (gf/tex)	0.5

chains is the most oxidizable polymer out of the other major commercial polyolefins, such as both low and high density polyethylene (PE).^{12,13}

The oxidative degradation processes are closely associated with the environmental condition. It may occur at all stages of the lifecycle of PP, including polymerization, storage, processing, and fabrication and in service. However, it is the most pronounced during the high-temperature processes used to produce the articles. This is due to the fact that the high-temperature processes are detrimental to the stability of the macromolecular structure and especially in the presence of molecular oxygen.^{12,13} In the present study, the production processes of the 3D nonwoven articles mainly consist of two steps: fiber deposition on the molds and through-air thermal bonding process. During the thermal bonding process, the hot air containing oxygen was used as the heating source. The fiber webs are subjected to the temperature above or close to the melting point of the PP sheath of the bicomponent fibers in the bonding chamber. Consequently, the PP sheath is likely subject to undesirable chemical changes caused by oxidation. These irreversible changes would result in alternation of physical and mechanical properties, and hence affect the performance of the produced articles. To predict the properties and/or control the quality, it is necessary to establish the relationships between the thermal bonding process conditions and the thermal oxidation degradation of fiber PP sheath for the thermally bonded nonwoven products.

The Fourier transform infrared spectra (FTIR) could highlight the presence of degradation products.^{8–13}

This technique is sensitive enough to detect the level of degraded polymers and suitable to investigate the thermal degradation mechanism of the fiber PP sheath in the thermal bonding process. The thermal analysis process is also generally combined with a change of mass and/or with thermal effects. Via thermal analysis these effects can be determined quantitatively, providing important information about the thermal stability of materials. During thermal analysis the samples are subjected to a controlled temperature program, during which the sample behavior is determined versus temperature or time. Thermal gravimetry (TG) determines temperature-dependent mass changes, while the differential scanning calorimetry (DSC) determines thermal effects.

In this paper, by means of the FTIR spectra and TG–DSC techniques, the thermal oxidative degradation of the PP sheath of the PP/PET bicomponent fibers during the thermal bonding process has been investigated. Emphases were placed on the mechanism of the thermal degradation and the effects of thermal bonding process conditions and the type of mold materials on the thermal degradation. The main objective of this study is to provide the necessary bases for optimizing thermally bonding process parameters to minimize the thermal oxidation of fiber PP sheath for the thermally bonded nonwoven products.

EXPERIMENTAL

Preparation of samples

The 3D nonwoven process has two sections: the web-forming system and bonding chamber. It has been described in detail elsewhere.^{6,14} In the present work, commercial polypropylene (PP)/polyester (PET) (sheath/core) bicomponent staple fiber was used and its properties are listed in Table I. Once the 3D webs are formed in the web forming system, they are moved out of the mold chamber across the machine width into a bonding section for consolidation. In the bonding chamber, the hot air is drawn through

TABLE II
Sample Codes and the Corresponding Bonding Conditions

Sample code	Mold materials	Bonding temperature (°C)	Dwell time (s)	Air velocity (m/s)	Fabric weight (g/m ²)
SBT1	Steel	144 ± 1	3 ± 0.5	4 ± 0.3	100 ± 1
SBT2	Steel	150 ± 1	3 ± 0.5	4 ± 0.3	100 ± 1
SBT3	Steel	154 ± 1	3 ± 0.5	4 ± 0.3	100 ± 1
SBT4	Steel	159 ± 1	3 ± 0.5	4 ± 0.3	100 ± 1
SDT1	Steel	150 ± 1	1.0 ± 0.5	4.0 ± 0.3	100 ± 1
SDT2	Steel	150 ± 1	3.0 ± 0.5	4.0 ± 0.3	100 ± 1
SDT3	Steel	150 ± 1	5.0 ± 0.5	4.0 ± 0.3	100 ± 1
NM1	Nylon	150 ± 1	3.0 ± 0.5	4.0 ± 0.3	100 ± 1
SM2	Steel	150 ± 1	3.0 ± 0.5	4.0 ± 0.3	100 ± 1
CM3	Copper	150 ± 1	3.0 ± 0.5	4.0 ± 0.3	100 ± 1

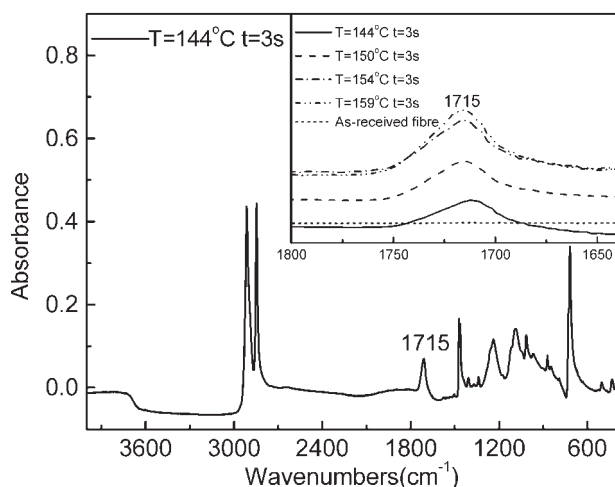


Figure 1 The FTIR spectra of the as-received fiber and the thermally bonded nonwoven samples produced at different bonding temperatures.

the fibrous web that is supported on the original mold. The hot air inlet is connected to hot air reservoir and duct heater through flexible adiabatic pipes. The air outlet is connected to the suction fan. An air guide is designed to improve the flow distribution around the web. The position of the air guide can be adjusted along the central axis.

In this study, three series of samples were prepared for the investigation of the level of thermal oxidative degradation of the PP sheath of the fiber. The molds were specially designed to improve the uniformity of the 3D web.¹⁴ Sample codes and the corresponding process conditions are listed in Table II.

Fourier transform infrared spectra

Infrared spectra were measured on both the as-received PP/PET bicomponent fiber and the nonwoven

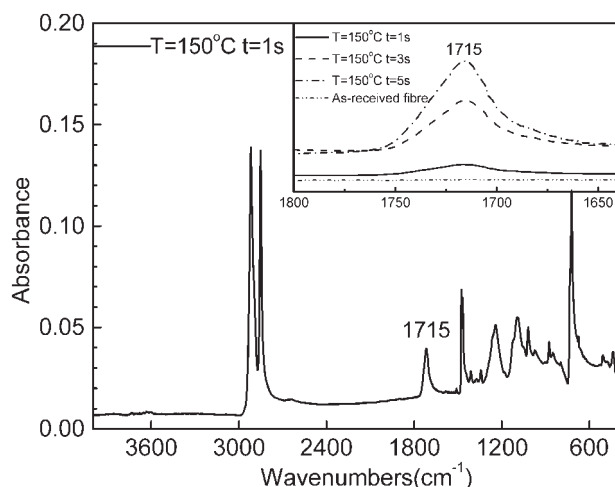


Figure 2 The FTIR spectra of the as-received fiber and the thermally bonded nonwoven samples produced using different dwell times.

samples. The measurements were carried out using the main bench and attenuated total reflectance (ATR) accessory of the Nicolet Magna-IRTM System 750 complete spectrometer, together with the Nicolet's OMNICTM software used to collect and process the data.

The spectra were recorded by plotting absorbance against wave number in the range of 400–4000 cm^{-1} and an average 100 scans at a resolution of 4 cm^{-1} . To correct for variations in sample thickness and gain a quantitative measurement of the absorbance intensity of the functional group, all absorbance measurements were normalized with respect to the absorbance peak at 974 cm^{-1} (CH_3 rocking band), which was used as a reference.

Thermal analysis

The thermal analysis tests were carried out on the NETZSCH Simultaneous TG-DTA/DSC apparatus STA 449 C/6/G Jupiter, using STA 449C on 18 TASC 414-4 acquisition software to record the data. The tests started from room temperature to 180°C, scanning at 3°C/min, and under air flow, on about 8 mg of the as-received fiber or the nonwoven samples.

For the thermal analysis tests, both the as-received fibers and the nonwoven fabrics were cut into small pieces, which were then spread on the bottom of an alumina crucible. To increase the resolution of the experiment, silicon oil was added to improve the heat transfer. The samples were weighed with an analytical balance (accuracy ± 0.01 mg), and the crucible and lid were cleaned with alcohol before use. Then the crucible was heated up to the final working temperature to burn out the solvents. When filling the crucible, no sample material might remain on the edge of the crucible, and then a needle was used to pierce one to five holes in the lid of the crucible to measure in defined atmosphere.

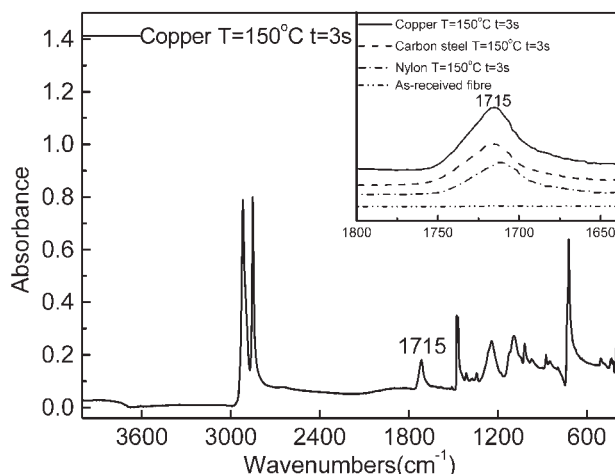


Figure 3 The FTIR spectra of the as-received fiber and the thermally bonded nonwoven samples produced using different types of molds.

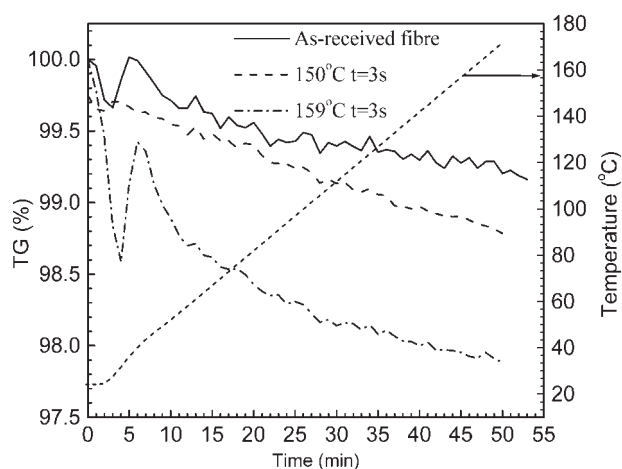


Figure 4 The TG curves for the as-received fiber and two thermally bonded nonwoven samples produced at different bonding temperatures.

For better thermostatic control, the thermostat was switched on overnight before measurement. When preparing the measurement, a series of parameters, such as calibration, sample weight, reference material, sample chamber temperature, temperature program, and atmosphere, were carefully considered and controlled. For example, a new calibration was done once there was any significant change in the measurement conditions. Good thermal contact between the samples and heat-flux sensor was an indispensable requirement for optimum results.

RESULTS

FTIR analysis

Earlier researchers^{12,13} show that the end product of the thermal degradation reaction is the oxidation of a polymer group, leading to the production of a carbonyl

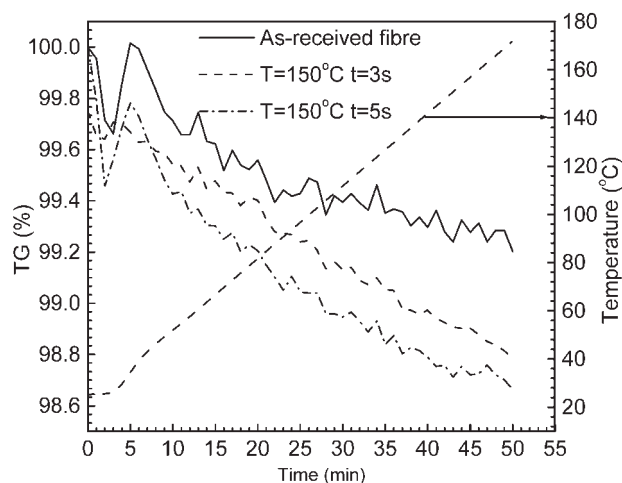


Figure 5 The TG curves for the as-received fiber and two thermally bonded nonwoven samples produced using different dwell times.

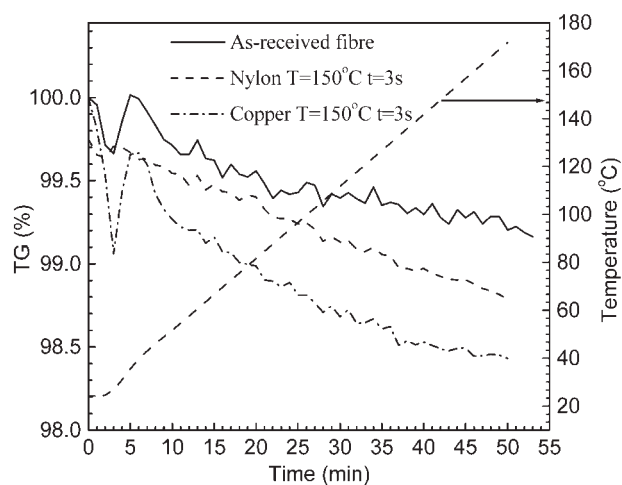


Figure 6 The TG curves for the as-received fiber and two thermally bonded nonwoven samples produced using different types of molds.

molecule. The presence of carbonyl groups shows up as absorption peaks in the range of $1690\text{--}1760\text{ cm}^{-1}$. An analysis based on such carbonyl peaks is the most reliable method to determine the level of the thermal degradation. The absorption peak height gives an indication of the degree of oxidative degradation.

Figures 1 and 2 present the FTIR spectra of the as-received fiber and the thermally bonded nonwoven fabrics produced at different bonding temperatures and different dwell times respectively. Clearly, both figures show that the 1715 cm^{-1} absorption peak of ketone, a type of carbonyl group, is present in all the thermally bonded nonwoven samples but for the as-received fiber. Such a 1715 cm^{-1} absorption peak of ketone is in a good agreement with that observed in the highly oxidized samples of unstabilized PP.¹⁵ The height of the 1715 cm^{-1} absorption peak increases with

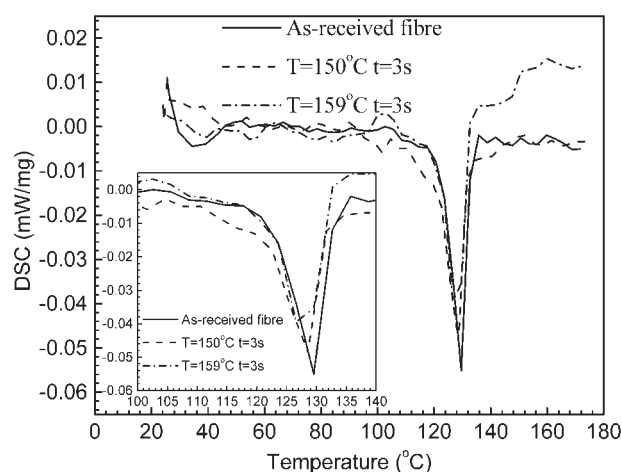


Figure 7 The DSC curves for the as-received fiber and two thermally bonded nonwoven samples produced at different thermal bonding temperatures.

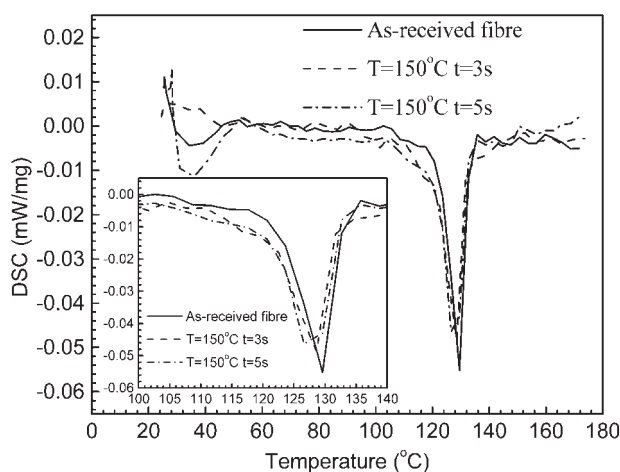


Figure 8 The DSC curves for the as-received fiber and two thermally bonded nonwoven samples produced using different dwell times.

increase in both the thermal bonding temperature and the dwell time. This is due to the increasing of concentration of ketone with increasing thermal bonding temperature and bonding time. Therefore, it leads to the conclusion that the level of thermal oxidative degradation of the fiber PP sheath increases with increase in the bonding temperature and dwell time.

The level of thermal oxidative degradation of fiber PP sheath in the thermally bonded nonwoven samples was also found to be affected by the mold material (Fig. 3). The height of the 1715 cm^{-1} ketone absorption peak increases with increase in the thermal conductivity of the mold materials, in the order: copper > carbon steel > nylon. Accordingly, the degree of oxidative degradation is highest for the sample produced using the copper mold, and is lowest for the sample produced using nylon mold.

TG analysis

Figure 4 shows TG curves of the as-received fiber and two thermally bonded nonwoven fabrics produced at different bonding temperatures. Clearly, the amount of weight loss depends on the thermal bonding temperature: a lower amount of weight loss corresponding to a lower thermal bonding temperature. Figure 5 indicates that the amount of weight loss for the thermally bonded nonwoven samples increases with increasing the dwell time. The type of mold material also significantly affects the amount of weight loss for the thermally bonded nonwoven samples (Fig. 6). The amount of weight loss increases with the thermal conductivity of mold materials. In addition, all the three figures also reveal that the amount of weight loss is clearly lower for the as-received fiber sample than those for all the thermally bonded nonwoven samples.

DSC analysis

Figure 7 gives the DSC heating curves, between room temperature and 180°C , of the as-received fiber and the thermally bonded nonwoven samples produced at thermal bonding temperatures of 150 and 159°C . It was reported¹⁶ that the melting point of a polymer varies with the amount of crystallinity. It decreases dramatically with decrease in crystallinity for polymers with lower crystallinities. A polymer with a particular crystallinity melts over a narrow range of temperature rather than at a distinct point resulting from variations in chain length. The temperature at the apex of the dip on a DSC scan was generally taken as the melting point for a given polymer.¹⁶ Clearly, the melting points of the thermally bonded nonwoven samples depend on the thermal bonding temperature. It shifts to lower temperature with increasing the bonding temperature.

Figure 8 indicates that the melting point of the thermally bonded nonwoven samples is also affected by the dwell time. A lower melting point corresponds to a shorter dwell time. Figure 9 reveals that the type of mold material also affects the melting point of the thermally bonded nonwoven samples. It can be seen from all the above three figures that the melting peaks of the thermally bonded nonwoven samples became slightly wider compared with that of the as-received fiber sample. Also, the melting points of the thermally bonded nonwoven samples decreased slightly with respect to that of the as-received fiber sample.

DISCUSSION

Mechanism of thermal degradation of PP

There is a wealth of studies on the thermal degradation of PP.^{8–13} It is well documented that the degradation of PP begins during the initial heat processing

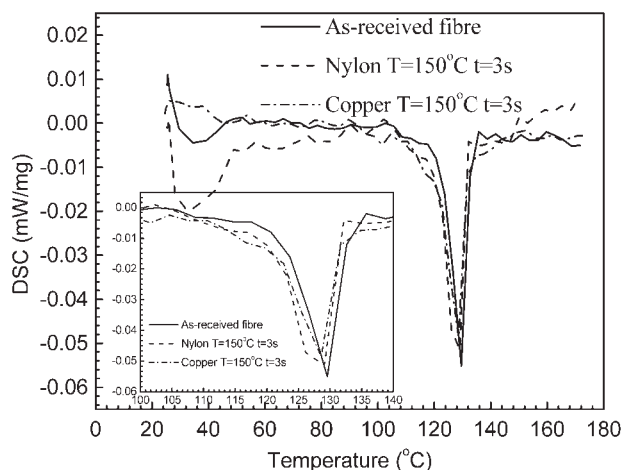


Figure 9 The DSC curves for the as-received fiber and two thermally bonded nonwoven samples produced using different types of mold materials.

stage of the product manufacture. If the molecular bond forces are exceeded then chain rupture will occur, this leads to the formation of chain radicals that initiates degradation.^{11–13}

The thermal bonding process was carried out in the presence of hot air (oxygen was present) and the PP was somewhat in a molten form; therefore, oxygen could diffuse into the PP. The thermal energy coming from hot air may result in chain breakage, e.g., chain scission, and hence yield the chain terminal radicals: free alkyl radicals R', which is probably the predominant degradation mechanism for the PP samples owing to the higher reactivity of the tertiary carbon based radical.^{8–13,17} The radicals could undergo further oxidative reactions in the presence of oxygen to form a peroxy radical ROO'. This abstracted a H atom from the polymer to form an alkyl radical and a hydroperoxide ROOH.^{12,13} These radicals, and indeed their neutral hydroperoxide (R-OOH), were short lived under thermal processing conditions and decomposed rapidly to the more stable alkoxy radical (RO) and the hydroxide radical (*OH). These very reactive radicals further abstracted hydrogen atoms from PP to yield new alkyl radicals R. Referring to the free radical oxidation model of polymers that was developed by Bolland and Gee,^{12,13} the thermal degradation of PP generally consists of the following three basic steps:

- i. Initiation: leading to the production of the first free radicals in the chain sequence
- ii. Propagation: giving the most important molecular product of oxidation and the hydroperoxide
- iii. Termination: eliminating the radical species.

The propagation step can be further expressed as:

1. $R' + O_2 \rightarrow R-OO'$
2. $R-OO' + RH \rightarrow ROOH + R'$
3. $ROOH \rightarrow RO' + HO'$
4. $RO' + RH \rightarrow ROH + R'$
5. $HO' + RH \rightarrow HOH + R'$

While the termination can be further expressed as:

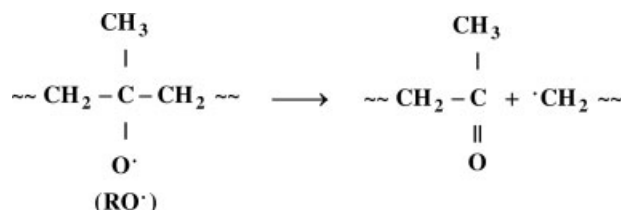
1. $R' + R' \rightarrow \text{Inert product}$
2. $RO'_2 + R' \rightarrow \text{Inert product}$
3. $RO'_2 + RO'_2 \rightarrow \text{Inert product}$

The exact degradation mechanism depends on the thermal bonding process conditions. However, the same chemical species are involved, including hydroxyl (OH) groups, carbonyl (C=O) groups and unsaturated (C=C) groups. The degree of degradation is often characterized by the major carbonyl peak typically centered around 1720 cm^{-1} . From the hydroxyl

and carbonyl groups, degradation products such as peroxides, alcohols, carboxylic acids, ketones, aldehydes, esters, and γ -lactones may be obtained by performing derivation reactions.

FTIR analysis

As shown in Figures 1–3, the infrared spectra of thermally bonded nonwoven products clearly show the presence of carbonyl absorption at 1715 cm^{-1} ¹⁵ in the thermally bonded nonwoven samples. This absorption band is associated with the development of a ketone following β -scission in PP, as expressed as follows:^{15,18,19}



As aforementioned, the thermal energy coming from hot air resulted in chain breakage, e.g., chain scission, and yielded the chain terminal radicals, which is the predominant degradation mechanism for PP samples. The higher the thermal bonding temperature is and the longer the dwell time is, the more energy is transferred to the fiber, leading to more chain breakage and more chain terminal radicals, and resulting in higher level thermal oxidative degradation of the fiber PP sheath.

In a similar way, during the thermal bonding process, when the samples were moved into the bonding chamber that was at a fixed temperature, a mold with higher thermal conductivity would be rapidly heated up to a higher temperature than a mold with lower thermal conductivity, given an approximately identical dwell time. Consequently, the samples on the former mold would have been held at the bonding temperature for a longer time than the samples on the latter mold would do. Therefore, the thermal oxidative degradation of the fiber PP sheath also increases with increase in the thermal conductivity of the mold material.

TG analysis

The observed weight losses in Figures 4–6 are also indications of the thermal-induced oxidative degradation of the PP fiber sheath. This is because for the fiber oxidation, there was first the build-up of a surface oxidized layer with oxygen grafting to the macromolecular network and some chain breaking reactions with the diffusion of volatile compounds out of the polymer.²⁰ The elimination of the volatile compounds would result in a weight loss.

The oxidation of semicrystalline polymer is not homogeneous, partly due to the heterogeneous nature of the solid polymer but also because oxidized region of the sample are more susceptible to further oxidation.²¹ The FTIR results reveal that the level of thermal oxidative degradation of the fiber PP sheath in the thermally bonded nonwoven samples increased with increase in the thermal bonding temperature, dwell time and the thermal conductivity of mold material. This agrees very well with the dependence of weight loss in the TG test on the thermal bonding temperature, dwell time and the thermal conductivity of the mold material. The weight loss of the as-received fiber sample was the least owing to the fact it did not go through the thermal bonding process prior to the TG test, therefore, it was less oxidized compared with the thermally bonded nonwoven samples. Consequently, it was less susceptible to further oxidation during the TG test, leading to less amount of weight loss compared with the thermally bonded nonwoven samples.

DSC analysis

The chemical alteration of the PP macromolecular crystal surface resulting from the thermal oxidative degradation of the fiber in the thermal bonding process probably increased the crystal imperfection, which was confirmed by the X-ray diffraction.¹⁴ The increased crystal imperfection shifted the melting point of the nonwoven samples to a lower temperature with respect to that of the as-received fiber samples. The higher the level of thermal oxidative degradation of the fiber PP sheath, the more was the decrease in the melting point. The DSC results are in good agreement with the FTIR and TG results.

The melting peaks of the thermally bonded nonwoven samples became slightly wider compared with that of the as-received fiber sample (Fig. 8). This may be due to the reduction in molecular weight and increase in polydispersity (wider molecular weight distribution) resulting from a chain scission degradation reaction in the thermal bonding process as aforementioned. The melting points of the thermally bonded nonwoven samples decreased slightly with respect to that of the as-received fiber sample (Fig. 9). This can also be explained as the chain scission process happened in the thermal bonding process. Upon the thermal bonding process starting, the fiber oxidative degradation developed and the oxygen-containing group content became high enough to render more difficulties to the interchain association, leading to a drop in T_m .

CONCLUSIONS

The FTIR results reveal that ketone developed in the thermally bonded nonwovens. The thermal deg-

radation of the fiber PP sheath followed β -scission oxidation mechanism in the thermal bonding process. The level of thermal oxidative degradation increased with increases in the bonding temperature, dwell time, and the thermal conductivity of the mold material. The TG results further confirmed this conclusion.

DSC analyses indicate that the melting peaks of the thermally bonded nonwoven samples became wider compared with that of the as-received fiber sample because of the reduction in molecular weight and increase in polydispersity (wider molecular weight distribution) resulting from chain scission degradation reaction in the thermal bonding process. The developed oxygen-containing group contents and increased crystal imperfection during the thermal bonding process caused the melting point of fiber PP sheath to decrease slightly compared with that of the as-received fiber.

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