

Effect of Heat-Sealing Temperature on the Properties of OPP/CPP Heat Seals. Part II. Crystallinity and Thermomechanical Properties

Tsujii Tetsuya,¹ Yasuo Hashimoto,² U. S. Ishiaku,³ M. Mizoguchi,³ Y. W. Leong,³ Hiroyuki Hamada³

¹PerkinElmer Japan Co. Ltd., 5-3 Toyotsu-chou, Suita-City, Osaka-Pref. 564-0051, Japan

²Fuji-impulse, Osaka, Japan

³Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

Received 18 March 2003; accepted 18 March 2005

DOI 10.1002/app.22443

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The crystalline structure of the heat-sealed part of oriented polypropylene (OPP) and cast polypropylene (CPP) films was investigated by differential scanning calorimetry, Fourier transform infrared spectroscopy, and thermal mechanical analysis (TMA). The relationship between the crystalline structure and the mechanical properties was analyzed. It was found that the high total crystallinity of both OPP and CPP gave rise to good mechanical properties and that the orientation of the crystalline structure in the OPP film also was an important factor. The

optimum condition for heat sealing was the temperature at which total crystallinity was highest while still retaining the crystalline orientation of OPP. The assessment of crystalline orientation by TMA is an innovation initiated by the authors. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 513–519, 2006

Key words: poly(propylene), orientation; mechanical properties; FTIR; differential scanning calorimetry (DSC)

INTRODUCTION

The laminate films used in packaging possess characteristics such as transparency, flexibility, and gas barrier properties or permeability, as the case may be. The application of films in packaging often involves sealing, for which several techniques are available.^{1–3}

Heat seals are made by applying pressure and heat, which melt the polymer films and subsequently lead to adhesion. The initial pressure enables intimate contact between the films. Adhesion is promoted by application of heat from the outside. As the sealant layer begins to melt, more intimate contact or wetting of the sealing surfaces occurs. Given sufficient time, molecular segments diffuse across the interface, forming entanglements, and thus seal strength increases.^{4,5}

Several studies of constant heat sealing have been reported in the literature^{7–13} Among other things, the studies considered the effects of jaw profile and temperature in oriented polypropylene film⁴ and measurement of interfacial temperature in LDPE.⁸ Mueller et al.⁴ studied the effect of platen temperature and dwell time in LDPE films and, among other things, determined the optimum temperature necessary to

form a good seal. They concluded that only at temperatures at which the higher-molecular-weight, less branched chains began to melt and diffuse across the interface could high peel strength be achieved. Sierra and Noriega⁶ investigated the phenomenological differences of the impulse heat sealing and constant heat sealing of PE. They found that the impulse heat sealing process is more sensitive to process parameters and configuration changes in sealing equipment than it is to film composition changes. However, studies of the effect of heat-sealing temperature on crystallinity will throw more light on the mechanical properties and morphology of heat seals. The first part of this study highlighted the effect of heat-sealing temperature on mechanical and morphological properties.¹⁴ In this follow up, the crystalline structure of the heat-sealed area was investigated and the relationship between the crystalline structure and mechanical properties was analyzed, particularly from the viewpoint of polymer processing. The heat-sealing procedure could be considered polymer processing as it imparts distinct characteristics.

EXPERIMENTAL

Materials

The plastic films used in this study were oriented polypropylene (OPP; OT, P-2161, Toyobo Co., Osaka,

Correspondence to: U. S. Ishiaku (umaru@ipc.kit.ac.jp)

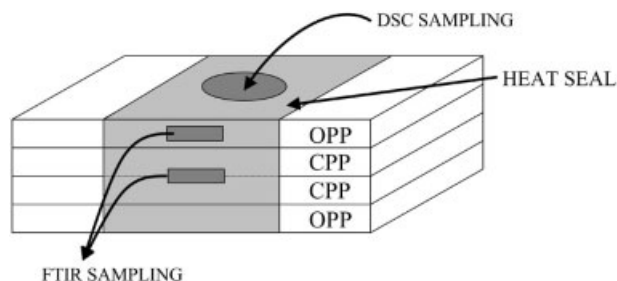


Figure 1 Sampling for DSC and FTIR.

Japan) and cast polypropylene (CPP; CT, P-1128, Toyobo, Co.). The films were laminated according to a dry laminate method using a urethane adhesive. This combination is commonly used in packaging materials and bags. Film thickness was 20 and 25 μm for OPP and CPP, respectively.

Heat sealing

The laminated films were placed in an impulse-type heat-sealing machine (Fuji Impulse, Ltd., Roosevelt, NJ) with both CPP sides facing each other. Stress and heat were applied through the machine. The temperature rose sharply in a very short period to the set temperature, at which it was maintained 0.1 s. It then decreased to room temperature within 5.0 s.

Temperatures in the regions in the two films being laminated and on the outside of the films were monitored by thermocouples. It was found that the peak temperature inside the laminated films did not rise to the set temperature and was approximately 20°C lower than the temperature applied outside the films in each case.¹ Nevertheless, in this study heat-sealing temperature refers to the set temperature applied to the outer surface of the films.

Differential scanning calorimetry

DSC was carried out with a Pyris 1 DSC (PerkinElmer, Wellesley, MA) with temperature increasing at 10°C/min from -20°C to 200°C under a nitrogen atmosphere. Samples were cut from the film as shown in Figure 1.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis was performed with a Spectrum One (PerkinElmer) FTIR analyzer equipped with an IR-microscope system (AutoIMAGE, PerkinElmer) at a resolution of 4 cm^{-1} and a scanning frequency of 128. Samples with a thickness of 10 μm were sliced from the film with a microtome cutter (HM350, MICROM). Figure 1 also shows the locations from which samples

were taken. The area analyzed was 10 \times 100 μm in size.

Thermal mechanical analysis

Thermal mechanical analysis (TMA) was carried out with a DMA7e (PerkinElmer). A compressing probe (ϕ 1 mm) made of crystal was used, and a load of 100 mN was applied perpendicular to the direction of the film. Disk-shaped samples cut out from the films and heat seals were used for testing. The heating rate was 10°C/min, and the scanning range was 25°C–200°C. A schematic diagram of the TMA testing is elaborated in Figure 2. The shrinkage that occurred when the film was heated could be detected, and a very small change in thickness was obtained.

Microwave molecular orientation

The molecular orientation of the OPP/CPP films at the heat seal and in the areas adjacent to the heat seal were measured using a Microwave Molecular Orientation Analyzer (MOA-6015, Oji Scientific Instrument, Hyogo, Japan). Two important parameters could be obtained through this analysis: the orientation angle and the molecular orientation ratio (MOR). Both parameters describe the extent of alignment of molecular chains with reference to the flow direction of the film. This is a new type of microwave instrument for quick determination of the molecular orientation and dielectric anisotropy of sheet materials. According to Osaki,^{15–17} it consists of a pair of rectangular wave guides, each partitioned by an iris plate. A given sheet is inserted into the gap and can be rotated around the axis normal to its plane. Polarized microwaves are irradiated perpendicular to the sheet, and the transmitted wave intensity is measured at every 1° of rotation angle as the sheet is rotated at a speed of 6.0 s per turn. This operation quickly gives information related to the molecular orientation of the given sample. Dielectric measurements can be made at any rotation angle, allowing the angular dependence of the real and imaginary parts of the complex dielectric constant and, thus, the dielectric anisotropy of the sheet to be

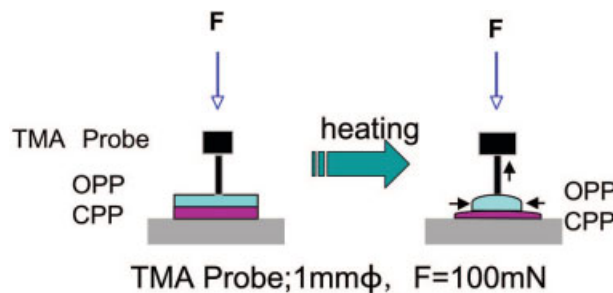


Figure 2 Schematic diagram of TMA testing.

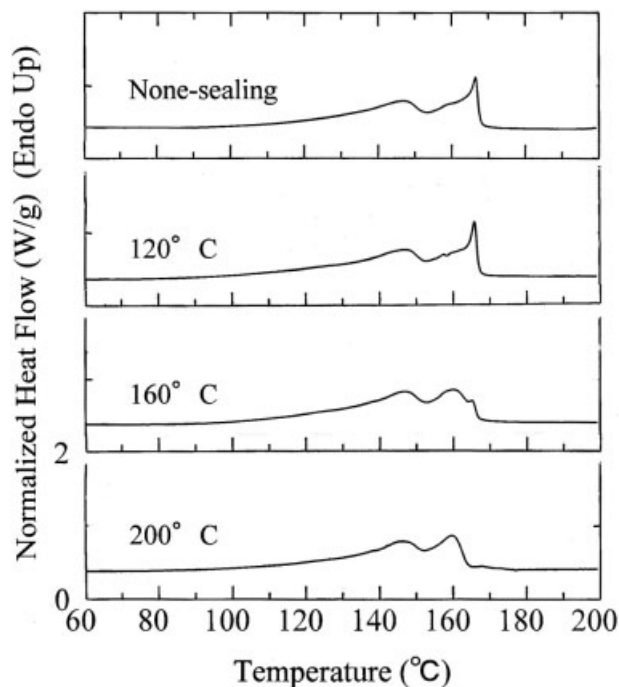


Figure 3 DSC curves of OPP/CPP heat seals for the respective heat-sealing temperatures.

determined in a few minutes. The angular dependence of the transmitted microwave intensity at a fixed frequency, that is, the orientation pattern, provides an orientation angle. The molecules in polymer films are arrayed on average in the direction specified by the orientation angle that has the smallest transmitted microwave intensity because of the shift of the resonance curve to the low-frequency side. The orientation pattern reflecting the dielectric anisotropy is very convenient for determining the orientation of molecules or fibers quickly and nondestructively.¹⁵⁻¹⁷

RESULTS AND DISCUSSION

Differential scanning calorimetry

A critical analysis of the DSC curves for the first run of OPP and CPP films revealed their distinct characteristics. For the CPP film, melting commenced at 80°C, and the curve rose gradually toward a broad peak at 146°C. For OPP, melting started at 140°C and culminated with a sharp peak at 167°C, followed by an abrupt decrease.

Figure 3 shows a comparison of the DSC curves (first run) of the non-heat-sealed laminated film and the heat seals produced at the respective temperatures. The curve for the non-heat-sealed laminated film shows two peaks that correspond to the melting peaks of CPP and OPP films at 146°C and 167°C, respectively. A similar configuration was maintained for the sample heat seals at 100°C and 120°C, at which

transformation to the broader melting peak centered at 160°C was complete. This indicates that orientation might have been relaxed but that the crystallinity of OPP was still retained. For the heat seals made at 140°C and 160°C, the peak at 167°C resulting from OPP film became smaller, decreasing further at higher heat-sealing temperatures until it disappeared completely at 200°C. This is an indication of the orientation of the OPP film being destroyed beginning from 140°C, and all traces of orientation disappeared completely at 200°C.

Figure 4 presents the relationship between heat of fusion and heat-sealing temperature obtained from DSC analysis. The heat of fusion was calculated from the area of the melting peaks. This heat of fusion represents the total energy required to melt both the OPP and the CPP films. The heat of fusion increased with increasing heat-sealing temperature until a maximum value was attained at 140°C, after which it decreased. This is similar to the changes shown in Figure 3, that is, beyond 140°C, the orientation of OPP was destroyed with an increasing heat-sealing temperature. The variation in orientation with heat-sealing temperature was verified with microwave orientation analysis.

Typical results from the microwave orientation analyzer as a function of heat-sealing temperature are presented in Figure 5. Figure 6 shows a comparison of the orientation angle between the non-heat-sealed and heat-sealed specimens according to their respective heat-sealing temperatures. The orientation angle represents the average alignment of polymer molecules in a particular direction. For OPP, the polymer molecules would usually align parallel to the flow or machine direction; hence, the orientation angle should have been close to zero (parallel to the vertical orientation axis). Good retention of orientation in the heat-sealed films could be seen with heat-seal temperatures from

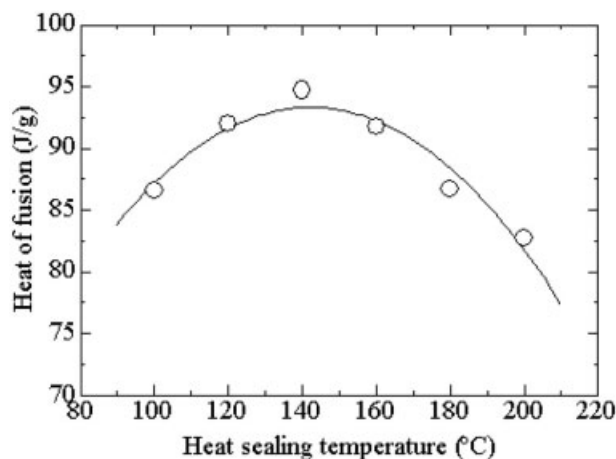


Figure 4 Relationship between heat of fusion and heat-sealing temperature.

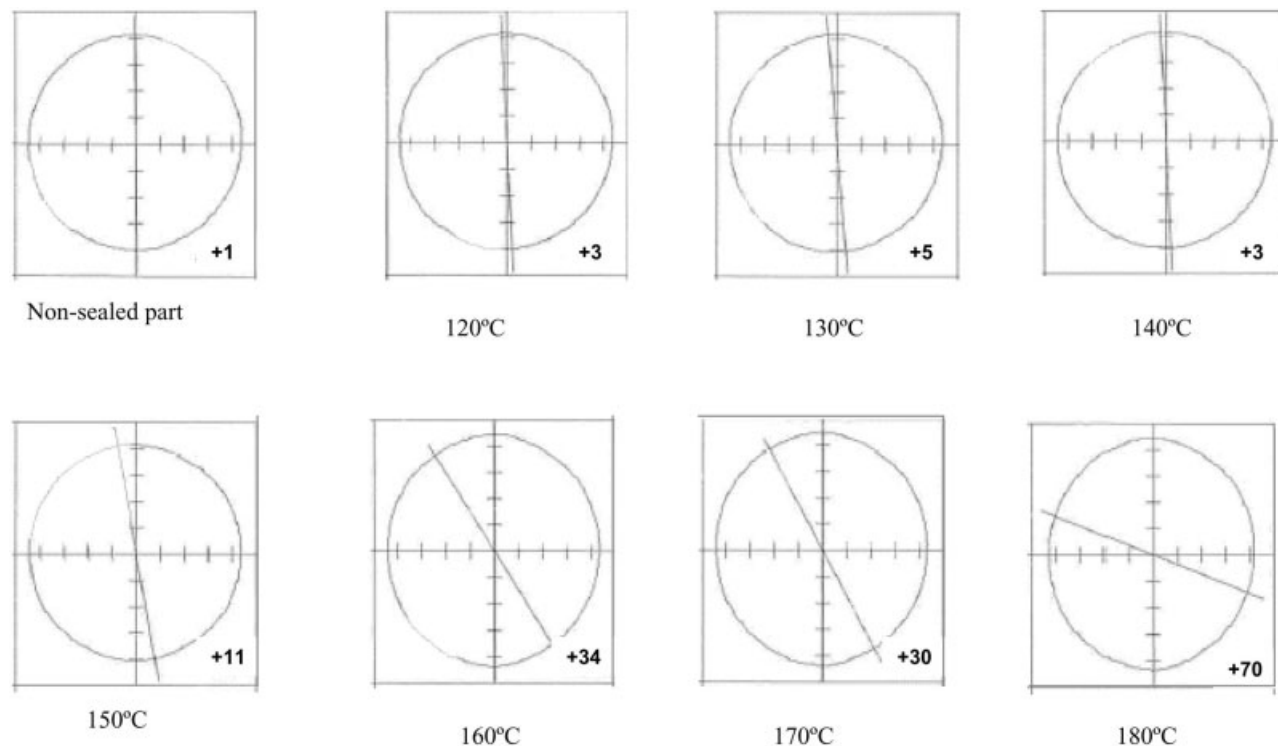


Figure 5 Typical microwave molecular orientation results obtained at different heat-sealing temperatures.

120°C to 150°C, above which the orientation angle diverted significantly from the vertical axis, indicating the point at which molecular chain movement had begun.

The molecular orientation ratio (MOR) values of the specimens, which indicate the density of chains orienting to the direction specified by the molecular orientation angle (MOA), are shown in Figure 6. It should be noted that the MOA only accounts for the oriented chains, whereas the MOR represents the relative number of chains that have been accounted for. The MOR values were consistently high at heat-seal temperatures of 120°C–140°C and drastically dropped at 150°C and above. This is a strong indication that many polymer chains in the OPP film had started to

lose some of their orientation beginning at 150°C, although a majority of the oriented chains still remained oriented parallel to the flow direction. High molecular orientation also was indicated by the low values of the MOA below 150°C. At higher heat-seal temperatures, both the distorted orientation axis (high MOA) and low MOR values pointed to severe loss in orientation because of the relaxation of molecular chains when sufficient energy was provided during heat sealing. FTIR imaging also was used to illustrate the loss of molecular orientation with increasing heat-sealing temperature.¹⁸

Fourier transform infrared spectroscopy

The FTIR spectrum of CPP film highlighting the peaks used to elucidate crystallinity is presented in Figure 7. The peak at 998 cm^{-1} can be attributed to crystalline structures, whereas that at 974 cm^{-1} is a result of amorphous regions. The ratio of the band intensities at 998 and 974 cm^{-1} gives an estimation of the qualitative crystallinity.¹⁹ The crystallinity values shown in Figure 8 are based on FTIR measurements. Figure 8 elaborates on the relationship between crystallinity and heat-sealing temperature for CPP and OPP films and heat seals. Non-heat-sealed OPP showed the highest crystallinity, which decreased with increasing temperature until 140°C. The crystallinity of OPP increased slightly with a further increase, so that a

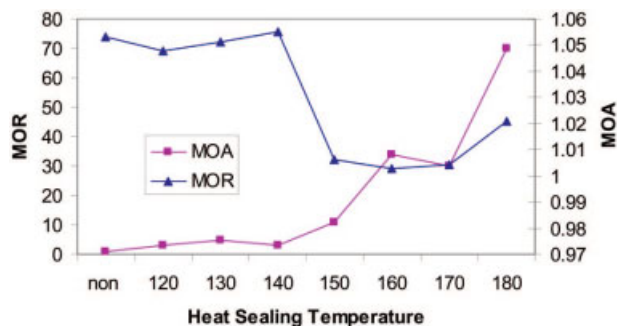


Figure 6 Molecular orientation ratio and molecular orientation angle as a function of heat-sealing temperature.

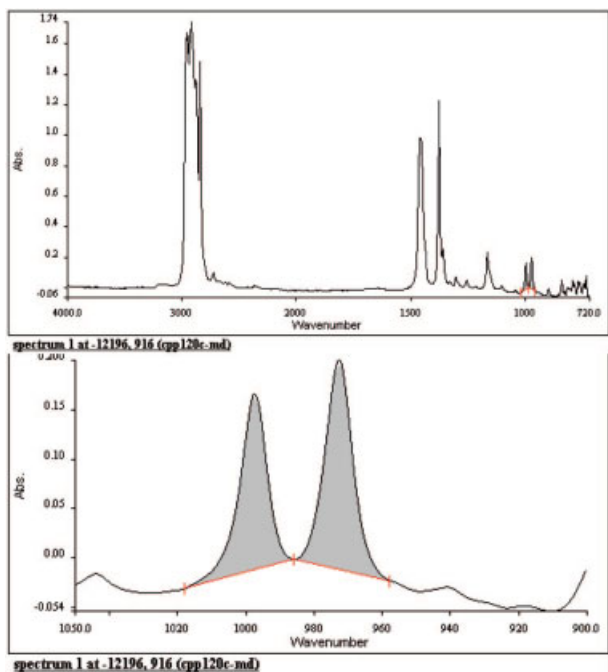


Figure 7 FTIR spectra of CPP film indicating the peaks used to evaluate crystallinity.

slightly higher value was found at 200°C than at 140°C and 160°C. This indicates that other types of crystallites were formed to replace the oriented ones. For CPP, the highest value was obtained at 120°C, followed by a gradual decrease with increasing temperature. Thus, it could be inferred that the amorphous content of CPP film increased with an increasing heat-sealing temperature after the maximum value. This increase in amorphous content, as well as the destruction of orientation, contributed to the decrease in mechanical properties discussed next.

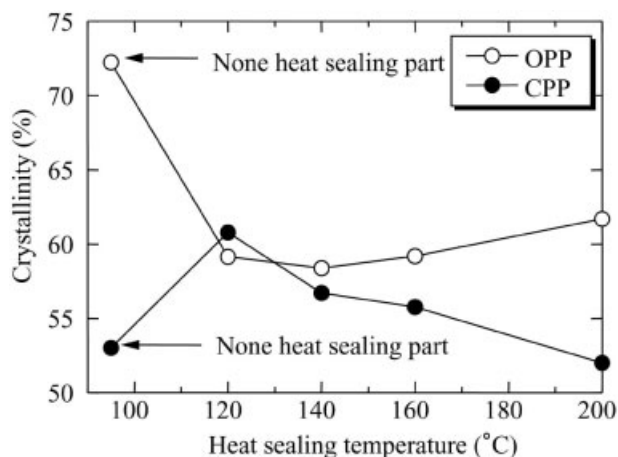


Figure 8 Relationship between crystallinity and temperature.

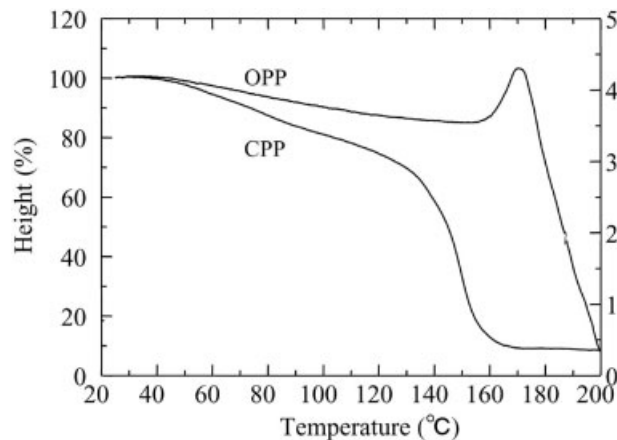


Figure 9 Comparison of TMA curves for OPP and CPP films.

Thermal mechanical analysis

Figure 9 shows the normalized height (thickness) of the CPP and OPP films obtained by TMA. For OPP, the height started to decrease at 40°C and continued to gradually decrease until a temperature of approximately 160°C, when the height increased sharply, reaching a peaked at 170°C. A sharp peak that appeared at 170°C in the corresponding DSC curve indicated the melting of OPP crystals (Fig. 3). As the crystalline structure started undergoing transformation at 170°C, a sharp peak appeared on the TMA curve because of the relaxation of orientation. Figure 2 shows that the OPP film is oriented laterally. Relaxation of orientation was accompanied by shrinkage (decrease in length) in the lateral plane with a simultaneous increase in height (increased thickness) vertically. The increased thickness translated to the observed peak. It is worth noting that the use of TMA to assess crystalline orientation in this fashion is an innovative approach initiated by the authors.

In contrast to the findings with OPP, CPP did not display such features because of a lack of orientation. The height of CPP film gradually decreased until 140°C, followed by an abrupt decrease. In the DSC curve, the peak was found at 146°C. Therefore, it could be inferred that when the crystalline collapsed during melting, no lateral shrinkage occurred, unlike OPP.

Figure 10 shows representative TMA curves of OPP/CPP heat seals produced at different temperatures. The curves may be grouped into three distinct types. In all cases, the height decreased gradually until 130°C, followed by a sudden drop, after which a sharp peak was shown for samples sealed at 100°C, 120°C, and 140°C, similar to that with the OPP film. This pattern of behavior is typified by the 100°C curve shown in Figure 8. Smaller peaks can be seen for the samples sealed at 160°C and 180°C, but no peak at all

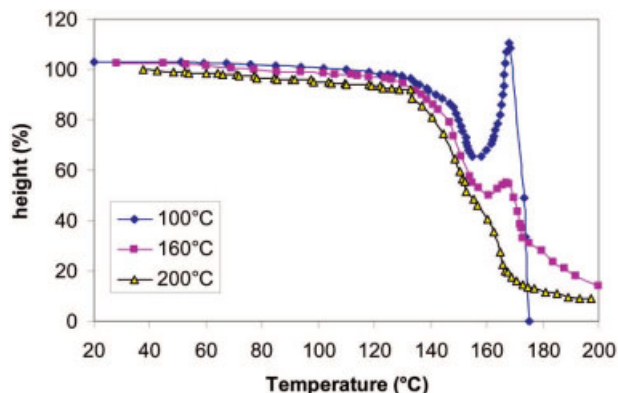


Figure 10 TMA curves of OPP/CPP heat seals produced at the respective temperatures.

for that at 200°C. This indicates that residual orientation of the OPP film was highest in the samples sealed at 100°C–140°C, whereas retention of orientation was less in the samples sealed at 140°C–160°C. The samples sealed at 200°C did not retain any of the original orientation of the OPP film, and hence no loss in orientation was detected during TMA.

These observations correlate well with the mechanical properties of the heat seals in the report on part I of this study.¹⁴ Here the effect of testing rate is shown in Figures 11 and 12. The general tendency was for tensile strength to reach its maximum at 120°C and to remain stable until 140°C, after which it decreased gradually to 160°C. Above a heat-sealing temperature of 170°C, tensile strength was consistently low until 200°C. It follows that maximum strength was displayed by the heat seals that retained the greatest orientation of OPP, whereas those heat seals with minimal or no orientation yielded similar, albeit low

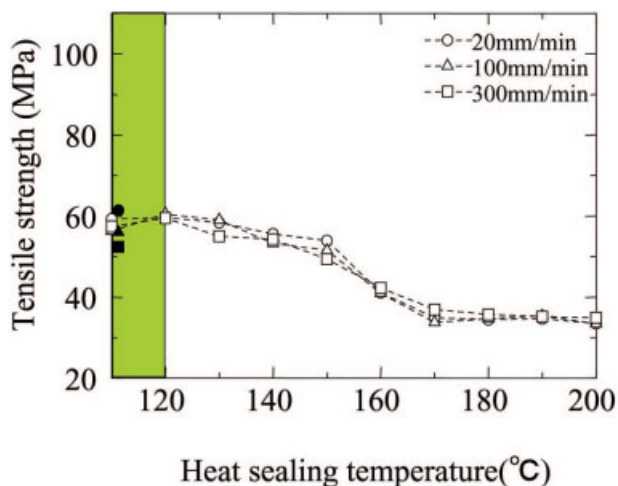


Figure 11 Relationship between tensile strength and heat-sealing temperature at different test speeds (20, 100, 300 mm/min) for MD samples.

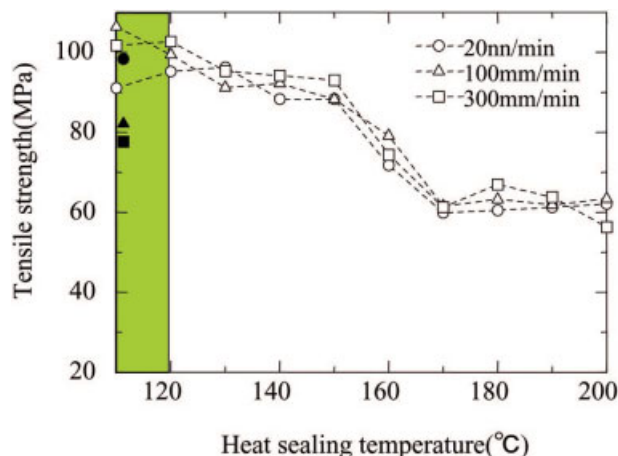


Figure 12 Relationship between tensile strength and heat-sealing temperature at different test speeds (20, 100, 300 mm/min) for TD samples.

mechanical properties. Bearing in mind that the crystallinity of CPP films was maximum around 110°C–140°C (Fig. 8), it can be safely inferred that optimum mechanical properties of the heat seals were governed by the maximum total crystallinity of both films, as well as by the retention of orientation. Both the MD and TD samples follow a similar trend regardless of testing speed. However, the MD heat seals generally were weaker in strength, as a comparison of Figures 11 and 12 shows. This is so because the machine direction for heat sealing was perpendicular to the molecular orientation of the OPP.

CONCLUSIONS

1. Crystallinity greatly affects tensile strength. When the crystallinity of CPP was highest, the tensile strength of the heat seals was at its maximum. Recrystallization occurred in CPP film heat-sealed at 120°C and above. Hence, increased tensile strength would be synonymous with enhanced crystallinity of CPP.
2. The extent of the molecular orientation in OPP and its relaxation behavior could be detected by TMA. The sharp peak related to relaxation of the orientation. Its disappearance with increasing temperature signified that the orientation was relaxed during the heat-sealing procedure at temperatures above 170°C. Hence, the low tensile strength at high sealing temperatures was synonymous with the relaxation of OPP during the heat-sealing process. Assessment of crystalline orientation by TMA is an innovation of the authors. The validity of this method is supported by well-established techniques such as microwave orientation analysis and FTIR imaging.

3. The heat-sealing condition that can provide a higher crystallinity of CPP while retaining the orientation in OPP would yield optimum mechanical properties.

References

1. Stokes, V. K. *Polym Eng Sci* 1989, 29, 1310.
2. Herrmann, T.; Lynch, B. ANTEC 2003, 2629.
3. Dixon, D.; Carangle, A. A.; McIlhagger, R.; McCracken, K. ANTEC 2003, 2629.
4. Mueller, C.; Capaccio, G.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 1998, 70, 2021.
5. Morris, B. A. ANTEC 2002.
6. Sierra, J. D.; Noriega, M. P. ANTEC 2003, 2623.
7. De Oliveira, L. M.; Faria, J. *Packaging Technol Sci* 1996, 9, 299.
8. Meka, P.; Sterling, F. C. *J Appl Polym Sci* 1994, 51, 89.
9. Sterling, F. C.; Meka, P. *J Appl Polym Sci* 1994, 51, 105.
10. Shih, H.; Wong, C.; Huang, C.; Wang, Y.; Wu, C. ANTEC 1998.
11. Montoya, N.; Sierra, J. D.; Noriega, M. P.; Osswald, T. A. ANTEC 1999.
12. Mueller, C.; Hiltner, A.; Baer, E. ANTEC 96 1996.
13. Halle, R. W.; Davis, D. S. ANTEC 1995.
14. Tetsuya, T. Ishiaku, U. S.; Mizoguchi, M.; Hamada, H. *J Appl Polym Sci* 2005, 97, 753.
15. Osaki, S. *Rev Sci Instrum* 1997, 68, 2518.
16. Osaki, S. *J Appl Phys* 1994, 76, 4323.
17. Osaki, S. *J Appl Phys* 1990, 67, 6513.
18. Hashimoto, Y.; Ishiaku, U. S.; Tsujii, T.; Leong, Y. W.; Hamada, H. *Polym Eng Sci*, submitted.
19. Gavrilu, D. E. *J Appl Polym Sci* 1996, 59, 71.