

Molecular Orientation Effect of Heat-Sealed PP Film on Peel Strength and Structure

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Abstract

Heat sealing properties are optimized by controlling temperature, pressure and dwell time, while film strength depends on the drawn ratio and the molecular orientation of the film. However, heat seal strength of polymer films with high drawn ratio shows lower peel strength, because the adhesion of films needs a higher heat sealing energy for molecular orientation relaxation at heat sealing. In the present study, polypropylene films with a drawn ratio of 1.0×, 1.5×, and 2.5× are heat sealed by using the heat sealing technique. The heat sealing condition is set to heat sealing time 1.0 s, sealing pressure 0.2 MPa, and heat sealing temperature 145°C. The effect of drawn ratio and stabilization temperature of PP films for peel strength are investigated using T-Peel test, DSC, FT-IR, and Raman spectroscopy. As a result, it is found that the peel strength is decreased with increasing the drawn ratio and stabilization temperature of PP films. The difference of ΔH and melting point from the result of DSC measurement are exhibited for 1.5× drawn ratio film as compared with 2.5× one. In addition, FT-IR imaging and Raman line mapping reveal the influence and variation of high order structure for heat sealed parts of the drawn PP films.

Keywords

Uniaxially-Extended Polypropylene, Molecular Orientation, Heat Sealing

1. Introduction

In recent years, plastic bags with heat-sealing are widely used in food packages, such as snack, retort pouch,

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frozen food, and so on. Heat seal technology is a very important technique for packaging industries because of keeping a long shelf life for food. Basically, there are two typical films, which are generally used, including laminated films and homo films. Heat seal is carried out by fusing the polymers through the application of heat and pressure. The initial pressure makes closely contact with both of film surfaces. Then adhesion is promoted by applying heat and pressure from the outside of films. The important factors to obtain great heat seal properties include heat sealing temperature, heat seal pressure, heat seal time and dwell time for a cool down after heat sealing. Many researchers have investigated about heat sealing time, temperature, and pressure to evaluate the mechanical properties of heat sealed parts of plastic bags [1]-[9].

On the other hand, film strength depends on the drawn ratio and molecular orientation of the film. The packaging film with high drawn ratio can be generally used for plastic bags which are required for high tensile strength, whereas the plastic film with a low drawn ratio can be made available for sealant layer, that is, OPP/CPP laminated film. However, to use chemical adhesion bond for laminated films is undesirable from a viewpoint of environmental load, while thermal laminated films or homo films are desirable as plastic bags in future. The heat sealing ability of higher molecular orientation films is poor due to loss of the heat sealing energy for the relaxation of oriented molecules in polymer films. Accordingly, it is very important to understand the relationship between heat sealing conditions, molecular orientation, higher order structure, stabilization temperature in polymer films in order to evaluate the difference of mechanical properties in heat sealed parts.

In this research, we use homo-polymer film specimens with the different drawn ratio in order to evaluate the effect of molecular orientation on heat sealed properties. The films are heat sealed with heat bar sealing machine at heat sealing condition, which is heat sealing time 1.0 s, heat sealing pressure 0.2 MPa and heat sealing temperature 145°C. The difference of higher order structure of the films is discussed on the basis of results of micro-Raman spectroscopy, FT-IR spectroscopy, DSC and tensile test.

2. Experimental

2.1. Materials

In this study, cast polypropylene (CPP) film (TOYOBO, PYLEN FILM-CT, P1011, Japan) was used as a base film. This CPP film was unidirectionally drawn at 1.0, 1.5, 2.5 times by uniaxial drawn machine (Nakamoto Packs Co., Ltd., Japan). At that time, these films were annealed at 80°C, 100°C, 120°C to stabilize molecular orientation and drawn film. The drawn film conditions then will be referred as 1.0×, 1.5×, and 2.5×, respectively.

2.2. Heat Sealing

Figure 1 shows a schematic diagram of heat sealing method in this experiment. The uniaxial drawn and un-drawn films were placed in a bar type heat-sealing machine (Heat seal Tester, Sangyo Co., Ltd, Japan). The heat seal pressure was kept constantly at 0.2 MPa. The heat sealing time was 1.0 second. The heat sealing temperature was set to 145°C.

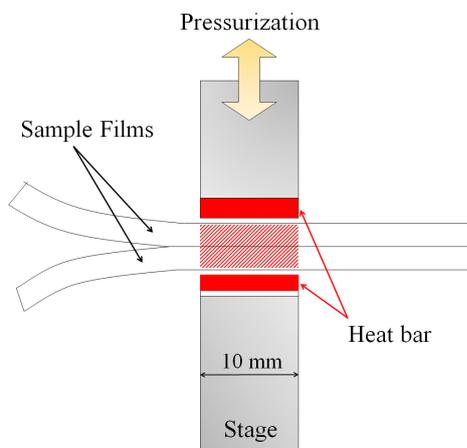


Figure 1. Schematic illustration of heat sealing process.

2.3. Peel Test

In order to examine the mechanical properties of the heat sealed part, a T-peel test was carried out with test pieces of 15 mm wide and 100 mm long. A schematic draw of the heat sealed specimen is shown in **Figure 2**. The peel test was performed at 300 mm/min by using an INSTRON universal testing machine (INSTRON 4466) at 20°C. The span length was 50 mm.

2.4. DSC Measurement

To examine the thermal properties of drawn sample films, a Differential Scanning Calorimeter (DSC) (Perkin-Elmer DSC, Pyris1) was utilized in the range of 40°C to 250°C at a heating rate of 20°C/min under a nitrogen gas purge. The temperature and heat of transition obtained by the instrument were calibrated with indium and zinc standards before the measurements.

2.5. Microscopic FT-IR Measurement

Heat sealed part of specimens were mapping by microscopic FT-IR (Frontier-Spotlight 400: Perkin Elmer, Japan) to evaluate the crystallinity and the orientation of heat sealed parts with and without heat sealing. Mapping mode was transmittance imaging method. Wave resolution was 4 cm⁻¹ with 2 scans. Pixel size was set to 25 μm.

2.6. Microscopic Raman Spectroscopy

Raman spectra have been measured with the micro-Raman backscattering geometry. The Raman spectra were excited with the linearly polarized 633 nm line of He-Ne laser (LabRAM HR-800: HORIBA Co., Ltd., Japan). The excitation beam was directed to the sample compartment of a properly modulated metallurgical microscope (Olympus BX-41). The microscope was used for the delivery of the excitation laser beam on the sample and the collection of the backscattered light through a beam splitter with objective lens adapted to the aperture of the microscope. Exposed time was set to 1.0 s. The number of scan was set to 5 times.

3. Results and Discussion

3.1. Effect of Stabilization Temperature of Each Drawn Film on Peel Strength

Figure 3 shows the peel strength of drawn film specimens at various stabilization temperatures. Peel strength of cast PP film was about 10 N. All of peel strengths for the drawn films indicated lower than that of cast PP film. The peel strength was decreased with increasing the drawn ratio for the PP film, while the peel strength was decreased with increasing the stabilization temperature for 1.0× and 2.5× drawn films although the peel strength of 1.5× drawn film was slightly increased with increasing the stabilization temperature. The peel strength for 1.5× drawn film showed around 3 N/15mm, while the peel strength for 2.5× drawn film showed about only 1

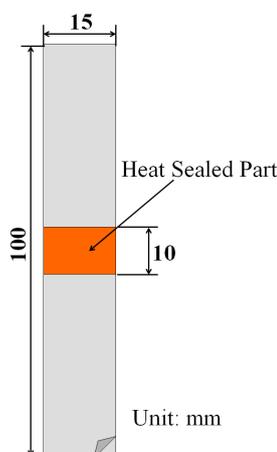


Figure 2. Schematic illustration of a specimen for peel test.

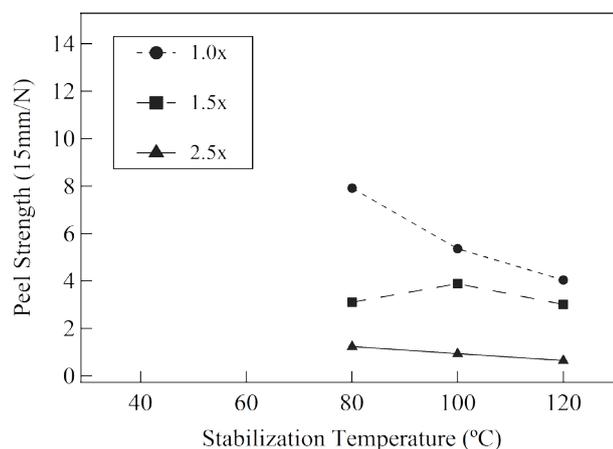


Figure 3. Peel strength of drawn film specimens for various stabilization temperatures at a heat sealed temperature of 145°C.

N/15mm, and the strength reduced to approximately 30%. This is caused by the high molecular orientation degree in PP film as compared with low drawn ratio films such as 1.0× and 1.5×. As a result, it was hard to heat seal for 2.5× drawn film. Thus, it is considered that there is a linear relationship between drawn ratio and peel strength, that is, depending on the orientation degree of PP molecules in the films.

3.2. DSC Measurement

We tried to perform DSC measurement in order to evaluate the change in crystallinity of higher order structure at heat sealed part of the PP drawn films. **Figure 4(a)** and **Figure 4(b)** shows the typically DSC curves of CPP film and 2.5× drawn PP film at 145°C heat sealing temperature, respectively. Melting temperature and melting enthalpy (ΔH) value of the 1st and the 2nd heating thermogram of CPP film are similar, while melting point of the 1st heating thermogram of 2.5× drawn film exhibited higher value as compared with the 2nd one. This difference depends on the drawn ratio of PP film, which influenced on differences in the molecular orientation of PP films. ΔH values of the films and heat sealed films at each heat sealing condition are shown in **Figure 5**. It was found that ΔH of non-heat sealed film was lower than heat sealed part due to a higher crystallinity of the heat sealed part as compared with the non-heat sealed part. In addition, ΔH of higher drawn ratio was lower than that of lower drawn ratio. It was attributed to the crystallization of the film after heat sealed. It can be considered that ΔH of higher drawn ratio film becomes low due to the energy waste to make it relaxation of the molecular orientation in PP films. Accordingly, these results will support the change in the secondary order structure of PP films. However, in the results of DSC measurement, it is very difficult to obtain the precise and information on secondary structure change in the edge area of heat sealed part. Hence, we applied the micro FT-IR mapping for heat sealed edge part of PP film for better understanding.

3.3. Microscopic FT-IR Measurement

Figure 6 shows a typical FT-IR spectrum of PP film. Generally, the 998 cm^{-1} and 841 cm^{-1} bands are associated with long repeating monomer units in the crystalline 3_1 helix of PP. The short helix segments are associated with the 972 cm^{-1} band of the FT-IR spectrum. There is a linear correlation between the intensities of the 998 cm^{-1} and 841 cm^{-1} bands and the density of PP as a measure of its crystallinity. Therefore, the crystallinity of PP can be determined by the ratio of the 998 cm^{-1} and 972 cm^{-1} absorption bands [10] [11]. **Figure 7** and **Figure 8** shows the CCD optical images and illustrate the FT-IR mapping images of PP film of heat sealed edge part. These mapping images were normalized at 972 cm^{-1} and imaged the peak ratio for 998 cm^{-1} /972 cm^{-1} as shown in **Figure 6**. The left area corresponds to non-heat sealed part and the right area corresponds to heat sealed part in each image in **Figure 8**. From the result, light color corresponds to the higher crystallinity area. In non-heat sealed part, crystallinity was increased with increasing the stabilization temperature so that the color variation is consistent with the molecular orientation of PP film. Because drawn film could raise the creep relaxation without heat stabilization after drawing. Therefore, crystallinity of non-heat sealed part of PP film was decreased

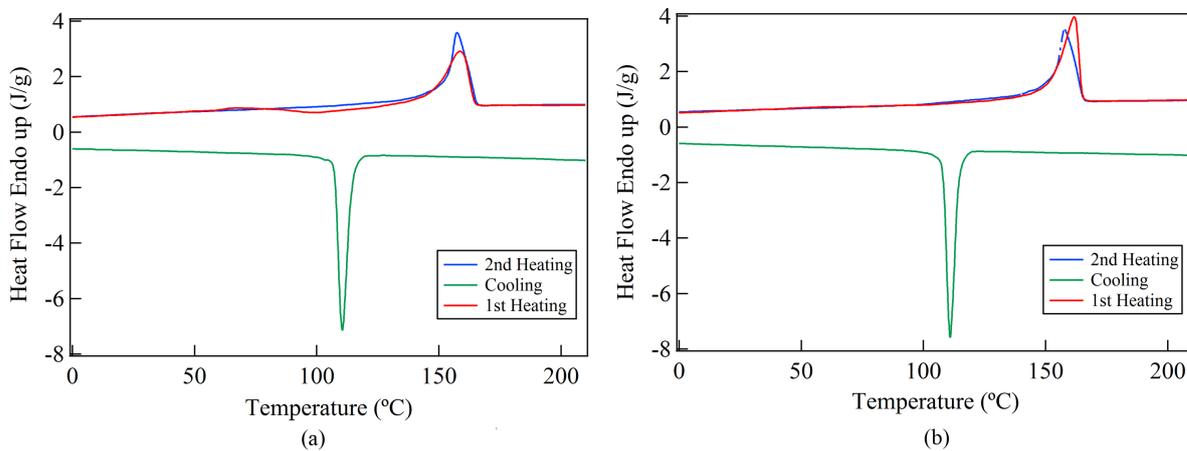


Figure 4. Typically DSC curves of (a) CPP film and (b) 2.5x drawn film at 145°C heat sealed temperature.

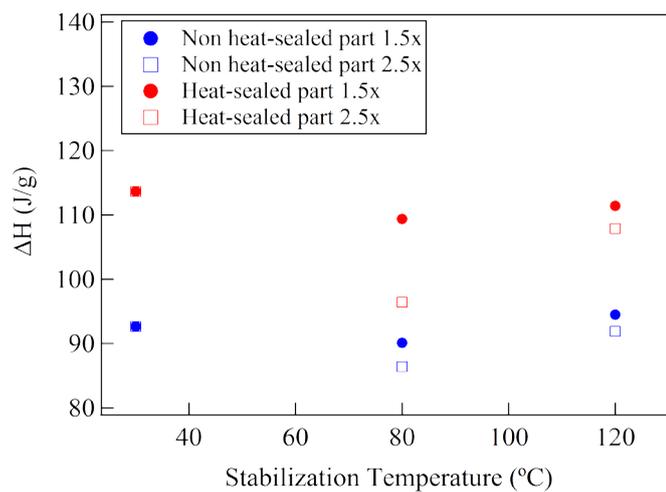


Figure 5. ΔH of various heat sealed PP films at 145°C for each stabilization temperature.

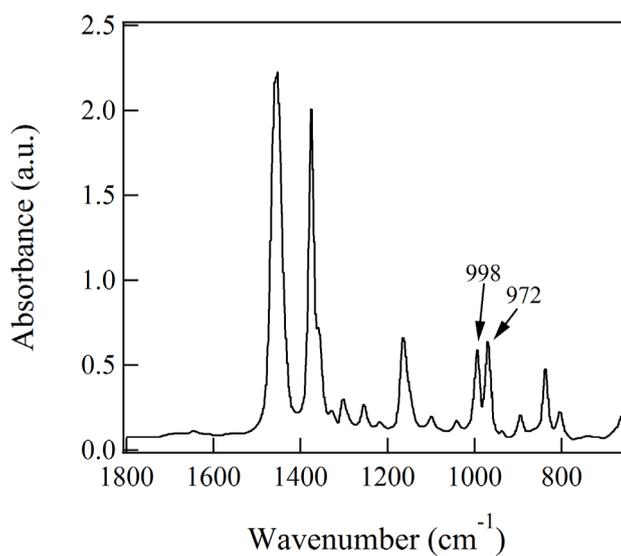


Figure 6. Typical FT-IR spectrum of PP films.

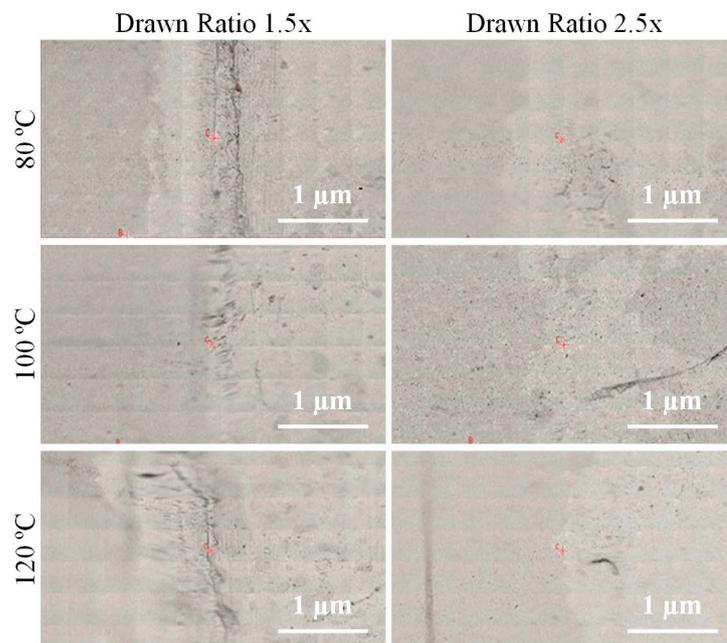


Figure 7. CCD images for PP films with drawn ratio 1.5× and 2.5×, heat sealing temperature 145°C.

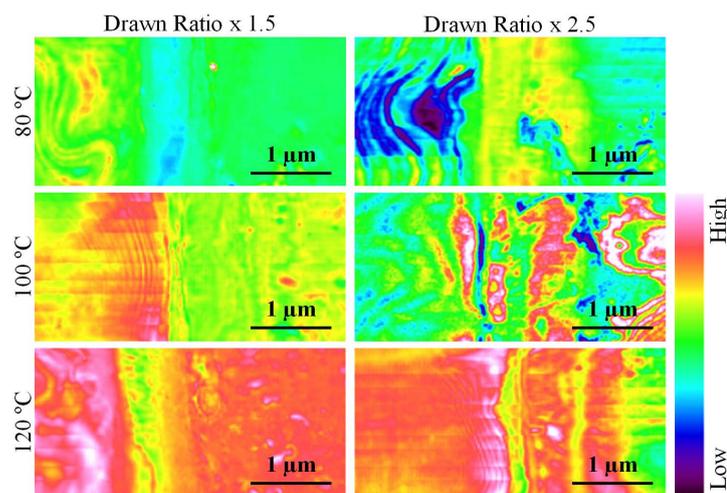


Figure 8. IR mapping results for PP films with drawn ratio 1.5× and 2.5×, heat sealing temperature 145°C.

with decreasing the stabilization temperature. On the other hand, similar tendency was shown in the heat sealed part of PP film, that is, crystallinity of heat sealed part was increased with increasing the stabilization temperature. However, in this case, it was seen that each crystallinity was lower as compared with non-heat sealed part. Because it is considered that the thermal energy of heat sealing is used for the relaxation of molecular orientation in PP films. As a result, the crystallinity of heat sealed part is lower than non-heat sealed part. In addition, the crystallinity of the edge part of heat sealing indicated the different tendency as compared with heat sealed and non-heat sealed part. It is very interesting and important phenomena of heat sealed films.

3.4. Microscopic Raman Spectroscopy

Figure 9 presents the Raman spectra of PP film for each drawn film. After drawing, some peaks were suppressed, where is considered that these peaks are corresponding to molecular orientation in PP films. In this

study, the peak ratio (I_{848}/I_{818}) was calculated in order to evaluate molecular orientation and/or crystallization changes near heat sealed edge part, and then the result was plotted in **Figure 10**. The peak ratio of neat film was higher than heat sealed part in **Figure 10(a)**. The slope of strength change was observed in the interface area within 200 μm . As the resolution and the pitch width of microscopic Raman spectroscopy are 1 μm and 1 μm respectively, it was found that the molecular orientation of PP films indicated the relaxation over an appreciable range of the slope gradually. It should be noted that when this slope is rapidly steep, stress concentration will arise at this edge part for tensile loading. In **Figure 10(b)**, the difference of Raman intensity was not indicated for each stabilization temperature, although the intensity at stabilization temperature 120°C became slightly coarse because of the relaxation of molecular orientation by the heat sealing energy. However, the degree of relaxation for 2.5 \times drawn film is very little as compared with 1.5 \times drawn film, and the heat sealing energy of 1.0 s and 145°C is insufficient to relax the molecular orientation of 2.5 \times film. As a result, it is clarified that the peel strength of the film indicated the low value as shown in **Figure 3**.

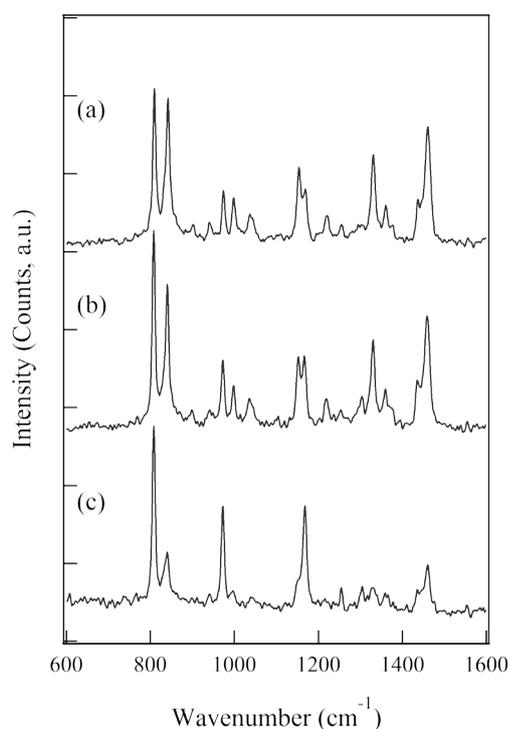


Figure 9. Typical Raman spectra of PP films with drawn ratio (a) 1.0 \times ; (b) 1.5 \times ; and (c) 2.5 \times .

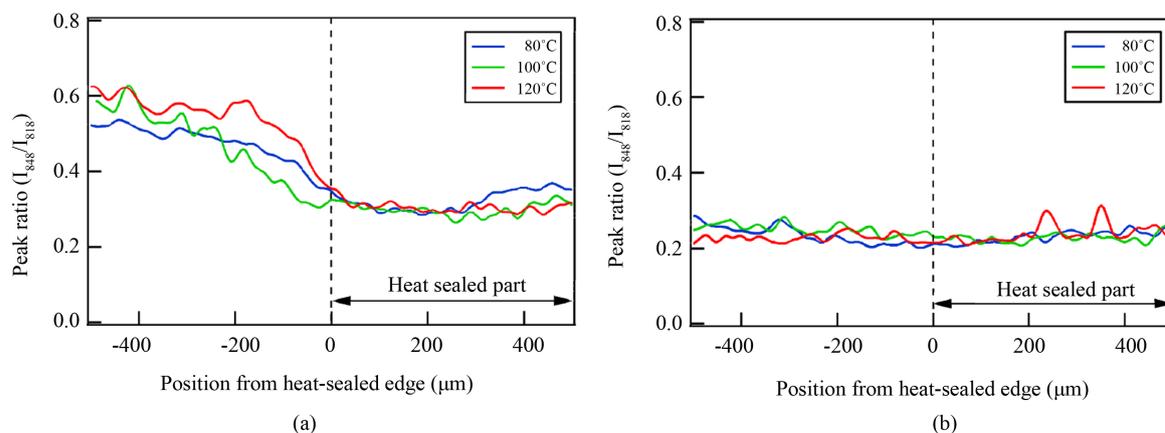


Figure 10. Raman line-mapping results for heat sealed films with drawn ratio (a) 1.5 \times and (b) 2.5 \times .

4. Conclusion

In this investigation, we investigated the effect of molecular orientation at heat sealed part of drawn PP film using T-peel test, DSC, micro-FT-IR, and micro-Raman spectroscopy. From these results, it was found that the peel strength was decreased with increasing the drawn ratio and stabilization temperature of PP films. In addition, the difference of ΔH and melting point from the result of DSC measurement were exhibited for 1.5 \times drawn ratio film as compared with 2.5 \times one. The reason why higher drawn film indicates the poor peel strength and low thermal changes was revealed the molecular orientation and relaxation of PP films by using FT-IR imaging technique and micro-Raman spectroscopy. It was suggested that we could analyze the very small area and changes on the basis of the results of heat sealed part using micro-FT-IR and micro-Raman spectroscopy imaging, which applied for drawn PP films. In the future, it was expected that the effect of heat sealing temperature, heat sealing pressure, kinds of film, and film thickness would be investigated at the heat sealed edge part in order to get the better packaging products.

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