Substrates Made of Simultaneously Biaxially Oriented PET Films for Printed Electronics

1 Introduction

Printed electronics are an area of great interest to the electronics industry sector for quite some time. Applications of printed electronics comprise RFID tags, sensors (e.g. for glucose meters), batteries, lightning and displays. Recent market forecasts predict a growth of the total market for printed, flexible and organic electronics from $16.04 billion in 2013 to $76.79 billion in 2023. OLED displays count for the predominent part of the turnover, with an increase from $10 billion in 2013 to more than $16 billion until 2015.[1]

The printing technologies described as novel these days however have their roots already in the beginning of the last decade. First patents describing the application of printed electronics to produce flat and flexible circuits have been issued around the 1920s[2]. In 1947 a publication of Brunetti and Curtis described a screen printing method for the production of printed electronic circuits[3]. The major benefit of printing electronics can be found in the possibility of producing microstructured layers in a simpler and cheaper manner compared to conventional electronics. Furthermore new functionalities like mechanical flexibility can be implemented.[4]

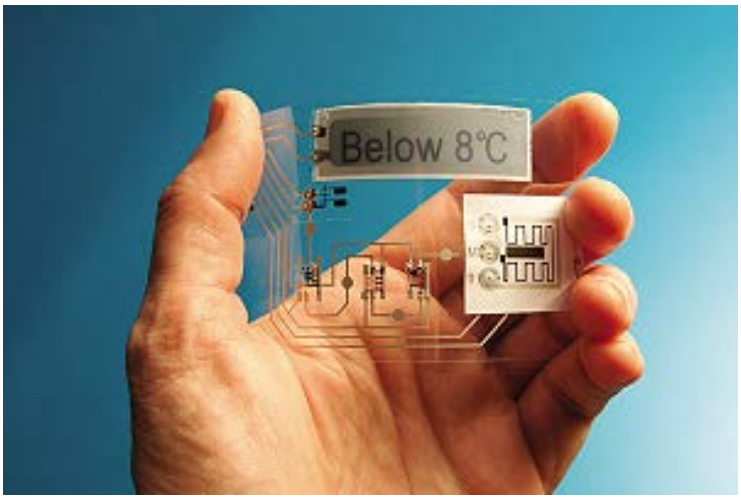

Figure 1: Flexible heat indicator and display[5]

[1] IDTechEx Market Research: Printed, Organic & Flexible Electronics: Forecasts, Players & Opportunities 2013-2023.

[2] Hanson, A., British Patent 4,681, 1903

[3] Cledo Brunetti, Roger W. Curtis: Printed Circuit Techniques. National Bureau of Standards, Circular 468, first issued 15 November 1947.

[4] Joseph Fjelstad: Flexible Circuit Technology, 4th Edition 2011.

[5] Source: www.newelectronics.co.uk/

Flexible printed circuits usually consist of an electrical conductive layer which is printed on a dielectric substrate. Printing technologies can be based on sheet-to-sheet (S2S) or on roll-to-roll (R2R) processes. S2S printing techniques like inkjet and screen printing are best suitable for low-quantity applications where high precision is required. For high-quantity applications like solar cells usually R2R printing techniques like flexographic or gravure printing techniques are used. Suitable conductive inks for inkjet printing are gold, silver and copper whereas copper and silver nanoparticles can be used for screen and flexographic printing. Proper substrate materials are films made of polyimide (PI), polyethylenenaphthalate (PEN) and polyethyleneterephthalate (PET). Due to its attractive cost / performance ratio silver or copper inks printed on PET substrates is a preferred setup for applications like membrane switch circuits (e.g. used in keyboards) and RFID tags. For that purpose e.g. silver ink is printed on a PET substrate and subsequently cured at temperatures between 100 and 120°C in order to reduce sheet resistance and thus to improve the conductivity.

Figure 2: Radio Frequency Sensor Tag for food chain and quality control[6]

A smooth surface and sufficient surface adhesion, low moisture absorption, good resistance to chemicals and solvents and high mechanical strength are required properties for substrates in printed electronics manufacturing processes. Moreover a low shrinkage at 150°C (ideally below 0,3 % in both directions) and a coefficient of thermal expansion (CTE) of 20 ppm/°C or lower is of particular importance in order to avoid dimensional changes and damages in the conductive layer during the thermal processing of the electronic circuit. Since the CTE and also the shrinkage of biaxially oriented PET (BOPET) films are widely depending both on the molecular orientation and on the morphology of the semicrystalline strucutre these properties can be strongly influenced and optimized by the simultaneous biaxial stretching process. Advantages brought by Brueckner's LISIM® technology in order to produce films with very low shrinkage has been demonstrated earlier.[7] In the present paper ways and possibilities for an optimization of the CTE using the LISIM@ technology will be shown.

[6] Source: www.foodproductiondaily.com/

[7] http://www.brueckner.com/en/brueckner-maschinenbau/technology-center/news-room/latest-news/pet-film-with-0-shrinkage-up-to-180c-by-simultaneous-stretching-with-lisimR/

2 Experiment

Two sets of simultanously biaxially stretched PET film rolls were produced on the pilot scale LISIM® line in the Technology Centre of Brueckner Maschinenbau GmbH & Co. KG.

Three BOPET film rolls (#1 - 3) were stretched simultaneously biaxially three times in machine direction (MD) and 3.4 times in transverse direction (TD) and subsequently heatset at different annealing temperatures (Table 1). Another five BOPET film rolls (#4 - #8) were stretched at different MD stretching ratios and subsequently annealed, whereas both the TD stretching ratio and the annealing temperature were identical for all samples (Table 2).

CTE measurements were carried by the LKT Erlangen using a thermal mechanical analyzer TMA Q400 from TA Instruments. Values were taken both parallel to MD and TD at the center position of the sample rolls. The dimensional change of the samples in the range between 25 and 60°C has been linearized and the CTE was given by the slope of the linearized curve.

Anisotropic refractive indexes where measured with an Abbe refractometer ED60 from Bellingham and Stanley using a linear polarizer in order to distinguish between refractive indexes perpendicular and parallel to the film plane respectively. Diiodmethane with a refractive index of 1.74 was used as a contact liquid.

Roll #	MD ratio	TD ratio	Annealing Temperature
1	3	3.4	180°C
2	3	3.4	210°C
3	3	3.4	240°C

Table 1: Simultaneous BOPET films annealed at different temperatures

Roll #	MD ratio	TD ratio	Annealing Temperature
4	3,2	3,0	210°C
5	3,6	3,0	210°C
6	3,8	3,0	210°C
7	4,0	3,0	210°C
8	4,2	3,0	210°C

Table 2: Simultaneous BOPET films stretched at different MD ratios

3 Results and Discussion

Figure 3 shows the CTE results for the films annealed at different temperatures. The graph shows an increase in the CTE parallel to TD for increasing annealing temperatures between 180 and 240°C. Parallel to MD however the CTE remains almost unchanged at annealing temperatures between 180 and 210°C. But when the annealing temperature is further increased to 240°C the CTE parallel to MD is also increased significantly. The increase in the CTE values with higher annealing temperatures is somehow unexpected because the annealing process usually results in a perfection of molecular order in the film plane due to thermal crystallization. This can be observed by the refractive index particularly parallel to TD which is increased from 1.6671 at 180°C to 1.6803 at 240°C.

Normally an increase in molecular alignment is supposed to result in a decrease of the CTE values because the CTE perpendicular to the molecular chain of the PET macromolecules is about 100 times higher than the CTE parallel to the chain direction. The reason for the increase in the CTE despite of a higher molecular orientation at higher annealing temperatures has to be found in the molecular rearrangement of tie molecules during the heatsetting process at temperatures above 180°C. The growth of the crystllites at the expense of relaxing and rearranging taut tie molecules decreases the molecular order in the non-crystalline regions. A secondary effect of the relaxation of taut tie molecules is the increasing brittleness of the films anneald at temperatures above 210°C. The difference in the behaviour of the CTE parallel to MD compared to TD can be found in the difference in the molecular order parallel to MD and TD caused by the unequal stretching ratios in these directions.

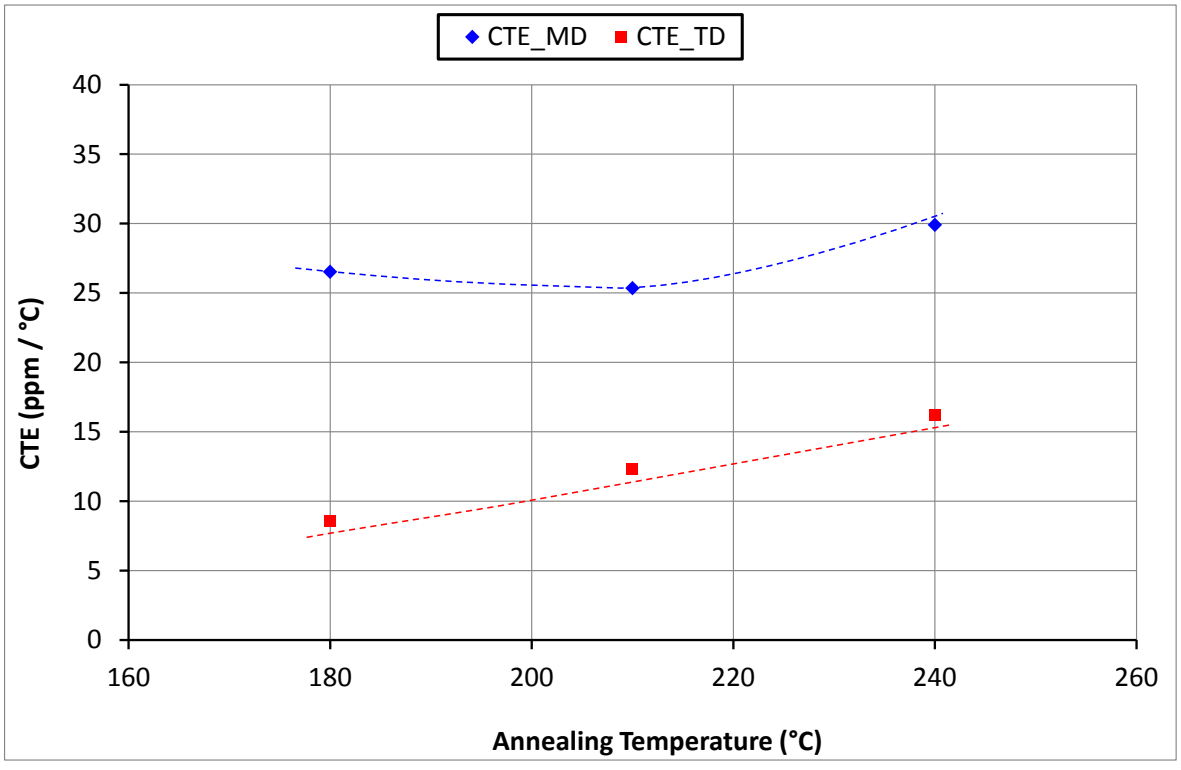

Figure 3: CTE results measured parallel to MD and TD for films annealed at different temperatures.

Figure 4 shows the decrease of the CTE parallel to MD with increasing MD stretching ratios up to 4.0. The decrease of the CTE is owed to the increase of the molecular MD orientation both in the amourphous and crystalline phase. A further increase of the MD stretching ratio over 4.0 seems to have no more orientational effect on the molecular network. Probably some disruptive orientation effects due to overstretching the molecular network the MD CTE value actually is increasing when the MD stretching ratio is further increased from 4.0 to 4.2. The CTE value parallel to TD remains almost unaltered despite the increase of the MD stretching ratio from 3.2 up to 4.0, but a further increase of the MD stretching ratio to 4.2 results also in an increase of the CTE parallel to TD. At that time there might occur a decrease in molecular orientation parallel to TD because of the disruption of TD oriented tie molecules in the amorphous regtions without further increasing the molecular orientation parallel to MD.

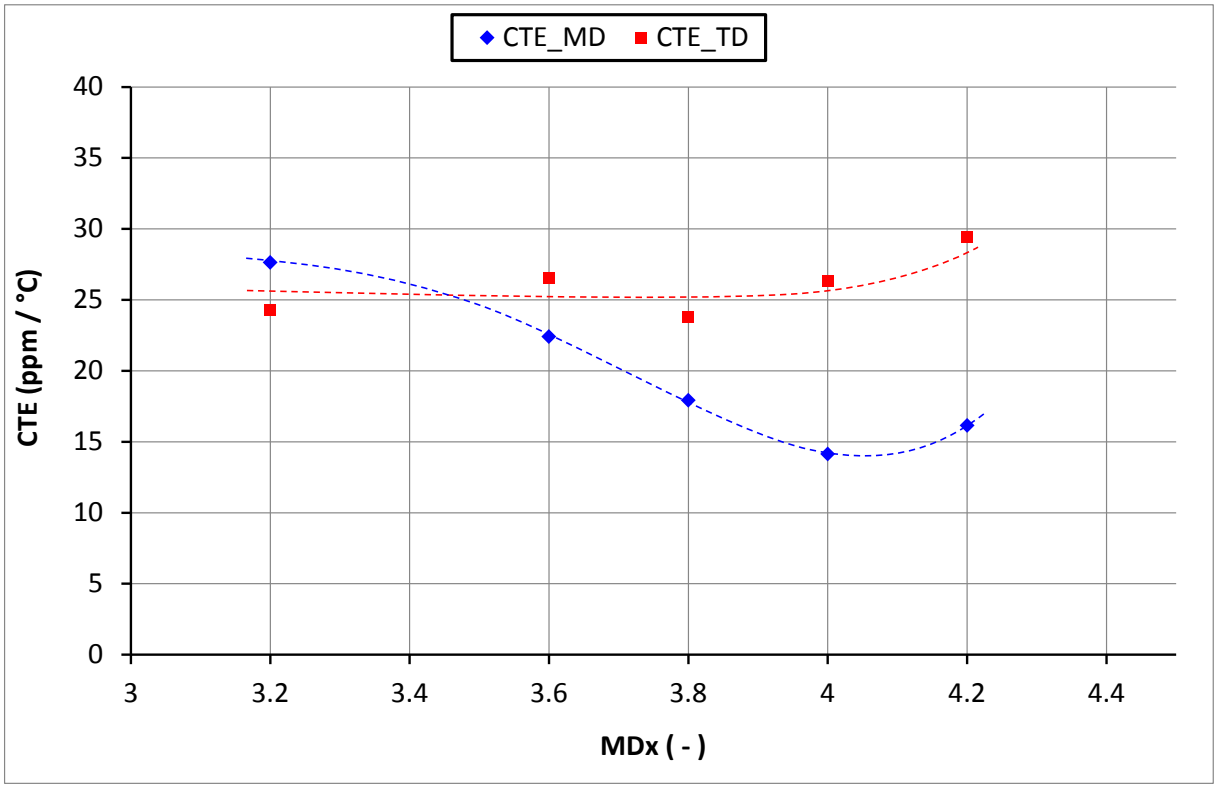

Figure 4: CTE results measured parallel to MD and TD for films stretched at different MD ratios.

4 Conclusion

As expected there is a huge potential to optimize the CTE through adjusting the stretching parameters such as stretching ratios and annealing temperatures in a simultaneous biaxial stretching process. For a minimization of the CTE in MD and TD it is necessary to adjust precicely both MD and TD stretching ratios. As could be derived from Figure 4 a MD stretching ratio between 3.8 and 4.0 combined with a stretching ratio slightly higher than 3.0 will lead to CTE values of 20 ppm /°C or below in both directions. This kind of molecular orientation can be hardly achieved by sequential stretching. The reason for that is that such a high molecular orientation parallel to MD caused by a high MD stretching ratio over rollers would cause a substantial strain induced crystallization and thus will result in massive problems during TD stretching. Moreover the disruptive effect of TD stretching in the sequential process would decrease the molecular order parallel to MD and thus lead to higher CTE values parallel to MD.

Also the minimization of the MD shrinkage in BOPET films that are supposed to serve as flexible substrates is only possible with the possiblity of an active MD relaxation given by the LISIM® technology without an excessive increase of annealing temperatures. As shown in the results above annealing temperatures have to be kept at 210°C or below in order to avoid excessive relaxation in the amorphous regions. Annealing temperatures at that level without mechanical relaxation of the film web usually result in shrinkage values of at least 2 %. Therefore the MD relaxation of the film web by means of a deceleration of the clips is unavoidable when shrinkage values of 0,3 % (150°C / 30 min) or below have to be achieved.

5 Summary

PET films have been stretched simultaneously biaxially at different MD stretching ratios and different annealing temperatures. The thermal expansion of the BOPET film samples parallel to MD and TD and also the refractive indexes of some selected samples have been analyzed. The advantages of Brueckner's LISIM® technology in order to optimize the coefficient of thermal expansion of BOPET films used as substrates for printed electronics applications has been shown.

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