



Surface Processing of Polyethylene Terephthalate for Orientation of Nematics in Display Devices

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Abstract. *Thermoplastic polymers have found widespread applicability in electronic industry owing to their facile processing and relatively low costs. Transparent polymer foils, like polyethylene terephthalate (PET), can be utilized in manufacturing components for liquid crystal display (LCD) devices. This work is focused on surface processing of PET through different procedures. The induced surface modifications of polymer samples were analyzed by optical microscopy. Contact angles of nematic drops on PET film are measured to evaluate how the method of surface modification reveals that the surface texturing affects the interactions of polymer with the liquid crystal. The influence of created surface anisotropy on the work of adhesion at polymer/liquid crystal interface is analyzed. Preliminary assessment of nematic orientation on the surface of modified PET foils is performed using polarized light. The results were discussed in regard with the used methodology to adapt the surface of the PET films to achieve optimal orientation of nematic molecules. The obtained data will open new perspectives on processing polymer foils as alignment layers used in LCD devices.*

Keywords: *polyethylene terephthalate, surface properties, liquid crystal*

1. Introduction

Polymers with good film forming abilities have been widely used in electronic industry as components for a variety of devices [1]. In particular, optically transparent polymer foils represent the ideal candidates for manufacturing flexible substrates for modern electronic viewing technologies, like flat-panel displays [2]. Such devices impose a periodic electronic refresh of the pixels to keep their state. A liquid crystal (LC) flat-panel screen contains thin layer of the nematic molecules, which is pressed between two sheets of transparent polarizing material deposited on conducting plates [3]. The top plate is basically a transparent electrode (*i.e.* Indium Tin Oxide) and the bottom plate must be illuminated to enable the observation of the images on the display. In the presence of electric signals, some segments of the LC layer can be activated, thus generating modifications in their light diffusing or polarizing characteristics. In this way, light can be either blocked or transmitted [4]. In the first case, no image is noticed, while in the second situation light passing through the nematic allows formation of an image on the screen [5]. The quality of the image is strongly affected by the uniform orientation of the nematic molecules [6]. For this reason, the material which comes in contact with the LC must have adequate surface properties to ensure a good alignment even in the absence of an electric field. This material is known in literature as alignment layer (AL) and generally consists in a transparent polymer foil with properly processed surface [7]. The most common methods to modify the AL surface are rubbing [8,9], stretching [10], photoalignment [11], low-energy ion beam bombardment at a glancing angle [12] and soft lithography [13].

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When placing nematic LCs on polymer surfaces with isotropic character, they tend to adopt a random orientation. Conversely, when the surface of the support is processed using one of the earlier mentioned methods, the director will be mainly oriented parallel to the deformation direction. The mechanism of nematic molecules arrangement on textured polymer substrates especially relies on geometrical factors rather than specific molecular forces [14]. The LC parallel alignment to the deformation direction can be explained by considering the additional elastic energy that would arise in LC as a result of the distortion in the vicinity of the grating-like wavy surface if the nematic was constrained with directors lying across, rather than parallel to, the support grooves/ridges.

The deep comprehension of the anchoring in LCs imposes profound knowledge of the interactions occurring at the textured polymer/nematic interface. The nature of these interactions involves van der Waals forces, steric interactions, chemical bonding and support surface topography [15]. A clear mechanism of LC orientation is not formulated. Therefore, another factor that could contribute to LC arrangement is the substrate surface wettability and anisotropy. Both aspects could be tested by means of contact angles, which will be different along and perpendicular to the grooves from the polymer surface.

Polyethylene terephthalate (PET) is a chemically stable thermoplastic resin, known for its great tensile strength, excellent optical transparency, good thermal stability and ease of processing. PET sheets are ideal for production of electrical components [16-18]. However, this hard material is less studied as orientation layer for LCs [19]. In a previous work [20], we showed that transparent polymer foils subjected to rubbing, stretching or both have a good potential in orientation of nematic molecules. Moreover, besides the uniform LC alignment, it is very important to achieve a good adhesion of the nematic on the modified surface of the polymer support [21].

This paper investigates the applicability of PET as orientation layer for flat-panel display devices. For this purpose, the surface of PET samples is modified through rubbing with a textile material, mechanical scratching with low roughness sand paper and patterning with wire brush. The resulted morphology is examined through optical microscopy. The balance between the adhesion and cohesion interactions at the polymer/nematic interface is evaluated by means of contact angle measurements. This reveals how the applied methodology of AL surface modification affected the adhesion of LC on the processed PET foils. A qualitative testing of the LC orientation on modified PET films is made using polarized optical microscopy. The results were discussed in regard with the used technique to modify the surface of the PET samples to attain optimal orientation of nematic molecules. The research from this work will open new perspectives regarding the processing polymer foils as ALs for flat-panel displays.

2. Materials and methods

2.1. Materials

The analyzed polyethylene terephthalate (PET) foils were cropped from clear and colorless glass bottles. The polymer films were further washed with distilled water and then dried in a vacuum oven for 6 hours.

The nematic liquid crystal used in this study is N-(4-methoxybenzylidene)-4-butylaniline (MBBA). It was purchased from Sigma-Aldrich and used as received.

2.2. Methods

The surface of the polymer films was modified by three approaches: (1) rubbing with velvet, (2) scratching with low roughness sand paper and (3) patterning with wire brush.

The morphology of pristine and modified PET samples was analyzed using a Bresser optical microscope in reflexion mode at a magnitude of 5x. Orientation of the nematic on PET supports was tested with the same device in transmission mode by placing the sample under crossed polarizers.

The contact angle measurements were performed on a laboratory made device at room temperature. The experiments were repeated seven-times on various zones of the samples.

The spectrum of the film sample in ultraviolet and visible regions was recorded on a SPECORD 210 PLUS device.

3. Results and discussions

The transparent PET foils were subjected to three methods of surface processing. The pattern created is correlated to the polymer substrate ability to generate uniform nematic orientation. A qualitative test of this phenomenon was performed using polarized microscopy. The anisotropy of the PET support was evidenced through contact angle measurements.

3.1. Spectral analysis

Optical transparency in visible domain is essential for the polymer alignment layers used in LCD devices. For this reason, the PET films chosen in the study were collected from clear plastic bottles. The transmittance of investigated plastic foil was measured in the wavelength interval of 300-1100 nm. Figure 1(a) indicates that the analyzed sample exhibits a transmittance of 84 % starting with 400 nm. This aspect is supported by literature data [22], which confirm the spectral absorption characteristics of colorless PET cut from plastic bottles. Figure 1(b) shows the image of the examined PET film. These alignment layers taken from recyclable sources present suitable optical features for the pursued application.

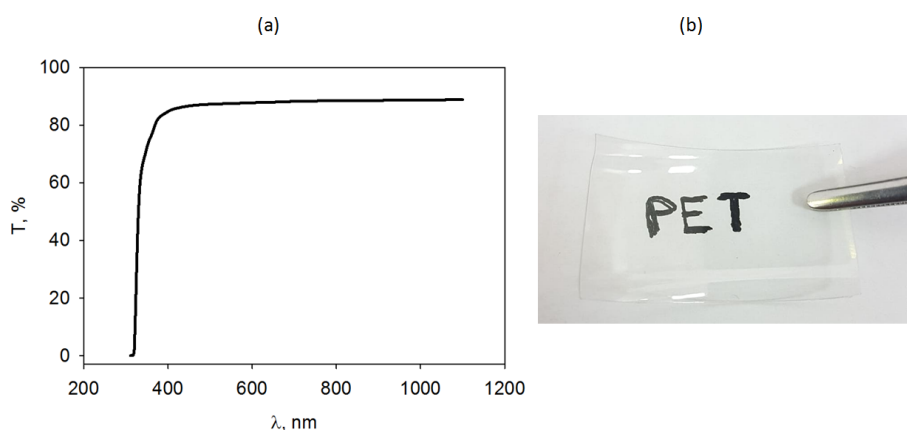


Figure 1. The UV - VIS spectrum of PET foil (a) and its picture (b)

3.2. Morphological analysis

Optical microscopy is a useful tool to monitor the morphology of polymers. The surface features of the pristine and modified PET films are displayed in Figure 2. Before application of any surface treatment to the PET samples, it can be noticed that the film surface is smooth without impurities. Similar results were reported by Ozaltin et al [23], which investigated PET films by scanning electron microscopy for biological purposes. Such polymer surfaces can be easily modified to achieve a proper topography that allows a uniform arrangement of the nematic molecules. In order to better observe the texture created on the PET surface through the three techniques, the morphology was recorded in reflected light.

First, the PET film was subjected to rubbing with velvet textile consisting of long and flexible acrylic fibers. In a previous work [24], these fibers were examined by scanning electron microscopy and it was proved that they have 4000 μm length and 23 μm thickness. As expected, the unidirectional contact of velvet textile with the PET foil led to a surface morphology consisting of fine grooves or striations (see Figure 2). They appeared along the rubbing direction as a possible consequence of alignment of PET chains at the film surface, combined with a good polymer ability to deform under loading. Literature [25] discusses the ductile character of PET under the influence of different factors, such as temperature and applied force. Thus, besides the created wave-like topography, it can be presumed that PET surface ductility enabled the deformation along the rubbing direction.

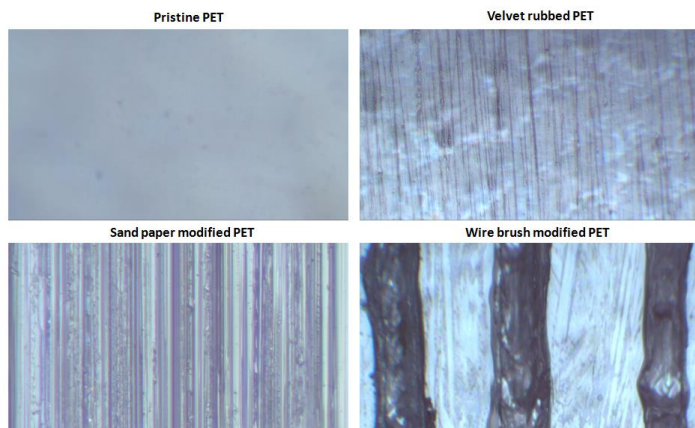


Figure 2. The optical microscopy images for the pristine and modified PET foils obtained with reflected light at a magnitude of 5x

In the second situation, the PET sample was processed by scratching with sand paper of low roughness. It can be noted in Figure 2 that the grooves created on polymer surface are deeper. This aspect could be explained by taking into account the higher hardness of sand paper comparatively with velvet textile, which is softer and consequently less penetrates the PET sample. Moreover, the surface of sand paper modified PET displays grooves with higher density.

In third case, the polymer substrate was processed with a wire brush. The latter is composed of several metal wires, which owing to their higher stiffness and hardness enter more deeply in the polymer bulk. The unidirectional deformation also induced the orientation of the macromolecular chains found in the vicinity of created grooves. This can be observed under the form of thin lines, which are formed between the prominent grooves generated by wire brush scratching viewed in Figure 2 as dark thick lines.

3.3. MBBA adhesion

The wettability characteristics of the polymer support are a key factor in establishment of the LC adhesion. For the unmodified and processed PET foils, contact angles measurements were performed. Several drops of MBBA in nematic phase were casted on the polymer substrates. The images of the LC contact angles on the PET samples are displayed in Figure 3. The pristine polymer has an isotropic character of the solid film surface as revealed by the contact angle values. For all modified PET substrates, it was noted a difference between the contact angle value recorded parallel to the surface grooves and that measured perpendicular to the surface texture.

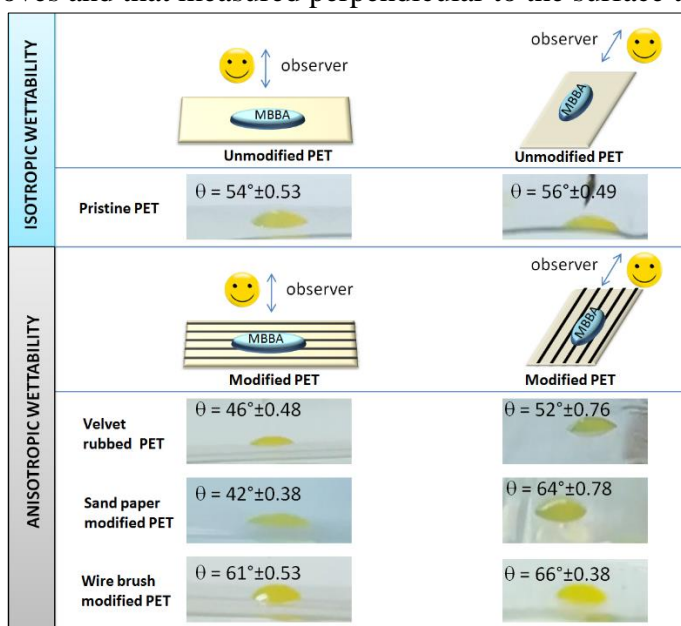


Figure 3. The MBBA contact angles and their standard deviations for pristine and modified PET films

The observed surface wettability of the MBBA on PET samples is important in evaluation of the LC adhesion behaviour. The latter is quantified by the work of adhesion (W_a), which indicates the intensity of the interactions at LC/polymer interface. The W_a parameter is defined in the equation (1) [26]:

$$W_a = \gamma_l(1 + \cos \theta) \quad (1)$$

where θ is the contact angle and γ_l is the surface tension of the LC.

Knowing the total surface tension of the used nematic [27], the MBBA adhesion interactions could be assessed and the corresponding results are listed in Table 1. To evidence the isotropic and anisotropic nature of surface wettability of pristine and modified PET films, the LC contact angles were measured in two situations: (1) drop orthogonal to the long axis of the topography (θ_{\perp}) and (2) drop parallel to the long axis of the topography (θ_{\parallel}). The pristine PET foil has almost the same contact angle and thus exhibits isotropic characteristics in terms of work of adhesion. Furthermore, it was remarked that the LC contact angle differs on the two considered observation directions, namely $\theta_{\parallel} < \theta_{\perp}$ and this impacted the values of W_a . Regardless the used surface treatment of PET, it was noticed that MBBA has stronger adhesion for θ_{\parallel} . Also, the nematic has the highest adhesion to the polymer supports processed by sand paper and velvet rubbing in comparison with the foils treated with wire brush. Therefore, it could be stated that Sand paper modified PET has the most pronounced surface anisotropy, which is would better support the MBBA orientation.

Table 1. The values and their standard deviations for the work of spreading of MBBA on pristine and modified PET films

Sample	W_a (mN/m)	
	θ_{\parallel}	θ_{\perp}
Pristine PET	53.99±0.25	52.90±0.30
Velvet rubbed PET	57.63±0.21	54.94±0.35
Sand paper modified PET	59.26±0.15	48.89±0.41
Wire brush modified PET	50.49±0.29	47.84±0.20

3.4. Testing of MBBA orientation

The processed surface of the PET films by the three methods was tested to verify if the created pattern is able to generate a uniform alignment of the MBBA molecules. For this purpose, a thin layer of nematic was deposited on the modified PET substrates and the prepared systems were closely examined by polarized light microscopy (Figure 4).

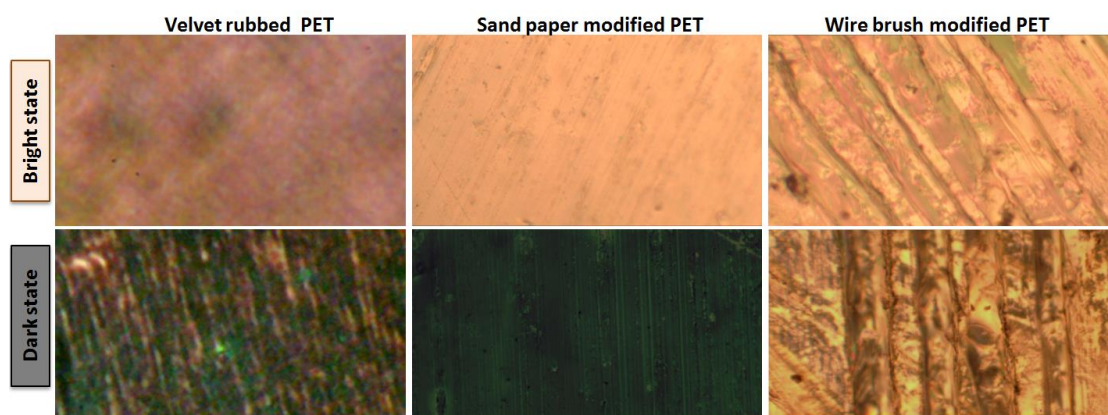


Figure 4. Polarized optical microscopy images for modified PET foils covered with MBBA molecules at a magnitude of 5x



Under crossed polarizers and in the absence of the sample, no light will be observed after the analyzer. When the polymer covered by the nematic is introduced on the microscope stage, the light will pass through it and will change the direction of polarization. In this case, the observer will see the radiations for which the electric field components have a projection on the analyzer transmission direction. The variations in intensity of transmitted light that were noted during rotation of the anisotropic sample under crossed polarizers provided valuable information on the quality of MBBA orientation on the processed PET supports. It was previously shown [20] that depending on the angle between LC director and transmission axis of the analyzer, one may observe dark or bright states. As noted in Figure 4, at an angle of 90° the light travelling through the sample is blocked. In this situation, the intensity of transmitted light is reduced and the observed image becomes dark. Instead, when the director of the MBBA molecules is rotated at 45° with respect to the transmission direction of the last polarization filter leads to a maximum light intensity (bright state). The amount of light leaving the analyzer is high because the projection of the electric field of incident light (passing along the easy direction of MBBA), along the analyzer transmission direction, is the biggest. These aspects are often remarked when homogeneous alignment of nematic molecules on textured supports takes place. In addition, as the contrast between the dark and bright states is higher it can be stated that the LC is uniformly oriented. Both dark and bright states were achieved for all processed PET substrates covered with nematic layer. The surface modification procedure with the wire brush leads to the weakest image contrast. This could be ascribed to the fact that the pattern created on PET foil is too rough and produces mainly surface scratching and less chain orientation. Thus, this surface topography tends to disturb the uniform arrangement of MBBA molecules. When rubbing PET with velvet, one obtains the smoothest grooves which allow better orientation of the LC. As a result the contrast between the dark and bright states is higher than that noted for wire brush processed system, but slightly lower comparatively with sand paper modified PET. In the latter case, PET develops deeper and denser grooves that enable a higher amount of MBBA molecules to align. Based on these tests, it could be concluded that the best LC orientation is attained when surface of PET foils is processed by rubbing with velvet and especially by treatment with sand paper.

4. Conclusions

The surface of PET film was modified by three techniques leading to a significant change of the morphological features, mainly viewed under the form of grooves or striations. Their depth and density is influenced by the hardness of the material that comes in contact with the polymer film surface. In order to evaluate the applicability of the modified PET foils as LC orientation supports, the wettability of MBBA was determined. It was observed a pronounced anisotropy in the values of the work of adhesion, regardless the surface processing technique. Sand paper treated and velvet rubbed PET films displayed the highest adhesion and anisotropy. These aspects supported a better orientation of the nematic molecules as revealed by polarized light microscopy experiments.

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