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Surface Energy of Polymer Substrates for Flexible Electronics: A Comparative Study of Polyimide, PET, and Ceramic-coated PET



Abstract: - Surface energy plays a crucial role in determining the adhesion, wettability, and overall performance of polymer films in various applications. In this study, we investigate and compare the surface energy properties of three widely used polymer films: Kapton polyimide, Tekra PET, and Novele (Ceramic coated PET). The surface energy of each polymer is characterized using contact angle measurements with different test liquids. Additionally, we explore the effects of various surface treatments on the surface energy of these polymer films. The results showed that Surface energy initially increases with plasma treatment but then stabilizes, a phenomenon analyzed in this study. This behavior is attributed to the interplay between functionalization and potential surface degradation.

Keywords: Printed Electronics, Flexible Substrate, Plasma Treatment, surface functional groups, Surface Energy

I. INTRODUCTION

Surface energy plays a critical role in determining the interfacial behavior and performance of polymer films in various applications. It directly influences adhesion to other materials, affecting bonding and durability [1]. Surface energy also governs the wettability of polymer films, determining the effectiveness / ability of inks and pastes to effectively spread and adhere to their surface [2]. Proper control of surface energy is essential in enhancing coating adhesion and uniformity on polymer films [3]. Moreover, surface energy is a key factor in the resistance of polymer films to environmental factors such as moisture, chemicals, and corrosion [4], significantly influencing their durability under these stressors.

Proper control of surface energy enhances adhesion between polymer films and other materials, such as coatings, adhesives, or inks [1]. Surface energy affects the printability and ink adhesion on polymer films, playing a vital role in packaging and graphic arts industries. In packaging; polymer films act as barriers against moisture, gases, and external contaminants, ensuring the integrity and shelf life of the packaged goods [5]. They contribute significantly to the safety and freshness of food products, pharmaceuticals, and other sensitive materials, thereby extending their usability [6]. In the realm of graphic arts, polymer films serve as essential substrates for various printing techniques such as flexography, gravure, and digital printing. Their smooth surfaces facilitate high-quality printing with precision and clarity, enabling the creation of intricate designs and images [7].

Modification of surface energy through techniques like plasma treatment or chemical functionalization allow tailoring of polymer film properties for specific applications [8]. Kapton (which is produced by condensation of pyromellitic dianhydride and 4,4'-oxydianiline) is a high-performance polymer known for its exceptional thermal stability, mechanical strength, and electrical insulating properties. It was developed by DuPont and is widely recognized for its use in aerospace, electronics, and industrial applications [9]. Kapton is valued for its ability to maintain its mechanical and electrical characteristics at elevated temperatures, making it suitable for applications in harsh environments such as space exploration, aviation, and electronic components [10]. Tekra PET, or polyethylene terephthalate, is a versatile thermoplastic polymer known for its transparency, dimensional stability, and barrier properties. PET is commonly used in packaging, labels, and graphic arts due to its excellent printability, optical clarity, and resistance to moisture and chemicals [11]. Novele, also referred to as ceramic coated PET, is a

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specialized variant of PET film developed by Novacentrix, which is used to improve adhesion and improve wettability. It is designed to exhibit enhanced electrical conductivity, making it suitable for applications in flexible electronics, printed circuitry, and wearable technology.

The objectives of the study are to characterize surface energy, determine and compare the surface energy properties of three polymer films, namely Kapton polyimide, Tekra PET, and Novele (Ceramic coated PET), using contact angle measurements with different test liquids and explore the effects of various surface treatments on the surface energy of the polymer films, aiming to understand how surface modifications can alter or enhance their surface properties. Then compare and contrast the surface energy values of Kapton polyimide, Tekra PET, and Novele (Ceramic coated PET), highlighting their distinct characteristics and potential advantages for specific applications. It is evident that plasma treatment increases surface energy; however, there hasn't been a comparative study directly assessing the changes in surface energy of three different flexible polymer substrates which are commonly used for printed electronics.

II. MATERIALS AND METHODS

In order to explore the contact angle of droplets (DI water and ethylene glycol) on various substrates, a HOLMARC contact angle meter (Model: H0-IAD-CAM-01A) was utilized to measure contact angles. Ethylene glycol was used because of its polar nature and ability to form hydrogen bonds. Droplets of DI water and Ethylene Glycol were applied to the sample surfaces using a 1.6 mm diameter syringe, with a consistent droplet volume of 1 microlitre and a flow rate of 50 microlitres per minutes. The contact angles formed between the droplets and the sample surfaces were recorded with precision using the contact angle meter. The photos for angle measurement were captured at least 10 seconds after placing the droplet on the surface, when there was no more spread of the droplet on the substrate. Each measurement was carried out five times to guarantee the accuracy of each test result. Additionally, surface modifications and enhancements to the materials' wettability were performed. Plasma treatment using plasma etch machine was employed to achieve this (Plasma Therm Unaxis 790 Plasma Etch system, CCP: Capacitively Coupled Plasma). The plasma treatment involved exposing the sample surfaces to ionized gases (99.99% pure oxygen, flow rate of 20 cm³/min), which increased their hydrophilicity and surface energy, making them more wettable. Careful control of the plasma etch parameters, such as gas composition, gas flow rate, plasma power, and treatment duration, was essential to achieve the desired surface alterations. Finally, the surface energy of the substrates was calculated using two components Wu model [12]. This technique is recommended for the determination of polymers and measurements are made with only two liquids [13]. When a drop of a liquid rest on a solid surface, it forms an angle θ with the surface, called contact angle. In thermodynamical equilibrium conditions, Young showed that:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta \tag{1}$$

where γ_S is the surface energy of the solid, γ_{SL} is the interfacial tension between the solid and the liquid, and γ_L is the surface tension of the liquid [14]. In this model, the surface energies of liquids and solids have been separated into two components, one called dispersive and the other polar with respectively for the liquid and solid phase a total surface energy:

$$\gamma_L = \gamma_L^d + \gamma_L^p \tag{2}$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{3}$$

$$\gamma_L \cdot (1 + \cos(\theta)) = 4 \cdot \frac{\gamma_L^d \cdot \gamma_S^d}{\gamma_L^d + \gamma_S^d} + \frac{\gamma_L^p \cdot \gamma_S^p}{\gamma_L^p + \gamma_S^p} \tag{4}$$

The calculation of γ_S^d and γ_S^p is done by solving a system of two Wu equations, one for each of the two liquids. The calculation of the polar and dispersive components is done on the basis of the measured contact angles, the polar and dispersive components of the surface tension and the total surface tension of two respective liquids. Table 1 lists the measured contact angle, polar and dispersive components of liquids A and B.

Table 1 Measured contact angle, polar and Dispersive components of liquids A and B		
	Liquid A (e.g. DI Water)	Liquid B (e.g. Methylene iodide)
Measured contact angle	θ_A	θ_B

Polar component	$\gamma_{LA}^p = 51.0 \text{ mN/m}$	$\gamma_{LB}^p = 2.3 \text{ mN/m}$
Dispersive component	$\gamma_{LA}^d = 21.8 \text{ mN/m}$	$\gamma_{LB}^d = 48.5 \text{ mN/m}$
Total	$\gamma_{LA} = 72.8 \text{ mN/m}$	$\gamma_{LB} = 50.8 \text{ mN/m}$

For more readability, intermediate coefficients are calculated:

$$A_A = \gamma_{LA}(3 - \cos\theta_A) / 4 \tag{5}$$

$$A_B = \gamma_{LB}(3 - \cos\theta_B) / 4 \tag{6}$$

$$B_A = \gamma_{LA}^p (\gamma_{LA}^d - \gamma_{LA}(1 + \cos\theta_A) / 4) \tag{7}$$

$$B_B = \gamma_{LB}^p (\gamma_{LB}^d - \gamma_{LB}(1 + \cos\theta_B) / 4) \tag{8}$$

$$C_A = \gamma_{LA}^d (\gamma_{LA}^p - \gamma_{LA}(1 + \cos\theta_A) / 4) \tag{9}$$

$$C_B = \gamma_{LB}^d (\gamma_{LB}^p - \gamma_{LB}(1 + \cos\theta_B) / 4) \tag{10}$$

$$D_A = \gamma_{LA} \gamma_{LA}^p \gamma_{LA}^d (1 + \cos\theta_A) / 4 \tag{11}$$

$$D_B = \gamma_{LB} \gamma_{LB}^p \gamma_{LB}^d (1 + \cos\theta_B) / 4 \tag{12}$$

$$a^p = A_B C_A - A_A C_B \tag{13}$$

$$a^d = A_B B_A - A_A B_B \tag{14}$$

$$b^p = B_B C_A - B_A C_B - D_A A_B + D_B A_A \tag{15}$$

$$b^d = C_B B_A - C_A B_B - D_A A_B + D_B A_A \tag{16}$$

$$c^p = D_B B_A - D_A B_B \tag{17}$$

$$c^d = D_B C_A - D_A C_B \tag{18}$$

The polar and dispersive components of the surface are solutions of the two respective quadratic equations by introducing the calculated coefficients. Table 2 lists the equations and solutions of the polar and dispersive components.

Table 2 Equations and solutions of the polar and dispersive components

	Resolution of the polar component γ_S^p	Resolution of the dispersive component γ_S^d
Eqn.	$a^p \cdot \gamma_S^{p2} + b^p \cdot \gamma_S^p + c^p = 0$	$a^d \cdot \gamma_S^{d2} + b^d \cdot \gamma_S^d + c^d = 0$
Solution 1	$\gamma_S^p = \frac{-b^p + \sqrt{b^{p2} - 4a^p c^p}}{2a^p}$	$\gamma_S^d = \frac{-b^d + \sqrt{b^{d2} - 4a^d c^d}}{2a^d}$
Solution 2	$\gamma_S^p = \frac{-b^p - \sqrt{b^{p2} - 4a^p c^p}}{2a^p}$	$\gamma_S^d = \frac{-b^d - \sqrt{b^{d2} - 4a^d c^d}}{2a^d}$

Two solutions are found for each of the polar and dispersive components of the solid. Only positive solutions are considered valid, as negative or complex values do not have physical significance in this context. Total surface tension (γ_s) is the sum of the two components [13]. Following the surface energy measurements of different samples under various treatments, the substrates underwent plasma treatment for 10 minutes at 250 W power. Subsequently, the contact angle of each substrate with a commonly used ink was monitored to assess the duration required for the substrate to recover from the plasma treatment effects. For the final assessment, the contact angle of the ink on each substrate was measured to determine the duration required for the substrate to recover from the effects of plasma treatment.

One of the most common methods for determining surface energy is the Zisman model[15]. This model suggests that the surface energy of a solid is similar to the maximum surface tension of a liquid that would create a contact angle of 0°, known as the critical surface tension. To apply this model, contact angles (represented as $\cos \theta$) of various liquids are plotted against their surface tensions. The plot is extended to determine the surface tension at

$\cos \theta = 1$, where $\theta = 0^\circ$, representing the surface energy of the solid. Although it is said that the Zisman model ignores the impact of polar interactions, it is only accurate for non-polar surfaces, here we just used this model to determine the surface tension from surface energy.

III. RESULTS

The results of the surface energy measurement are shown in Fig 1. As can be seen, surface energy (mN/m) of the substrates after various plasma powers and times are shown. As evident from the analysis of the results, the surface energy of the substrates increases after plasma treatment. However, as time and voltage increase, the diagram shows a plateau. For a better understanding of the surface changes before and after plasma treatment, SEM images of the Kapton samples' surfaces are presented in Fig 2. Also contact angle and accordingly surface energy measurement was performed 1 week after the plasma treatment, as it is claimed that the effect of surface treatment will completely disappear after 72 hours [16]. The contact angle of the various substrates and silver ink was measured on different days, and the results are depicted in Fig 3.

IV. DISCUSSION

The surface energy of polymers change after plasma treatment due to the alteration of surface chemistry and morphology caused by the energetic ions and radicals present in the plasma [17]. As shown in Fig 2, there is a slight change in surface morphology, which appears to have no significant effect on the contact angle. Contact angle of the samples after 1 week showed the same amount as before plasma treatment, indicating that the minor change in morphology does not impact the contact angle or surface energy. To be more specific, by ion bombardment of the surface during plasma treatment, surface will be subject to nanometric change, which is minuscule and microscopic compared to the droplet utilized for contact angle measurement. Consequently, these alterations cannot account for the change in surface energy, as evidenced by the consistent contact angle measurements obtained after one week, during which time any other effects of plasma treatment dissipate [16].

Plasma treatment introduces polar functional groups onto the polymer surface and enhancing its wettability [18]. The incorporation of polar groups increases the polar component of surface energy, leading to a decrease in contact angle values [19]. Increasing the polar component of the surface leads to increasing the surface energy [20]. Additionally, plasma treatment can remove contaminants and low-energy layers from the surface, exposing fresh polymer chains with higher surface energy. The changes in surface energy after plasma treatment play a crucial role in improving adhesion, coating uniformity, and overall material performance [21].

On the other hand, the changes in surface energy of tested polymers are connected by another parameter. Increasing plasma power and time can be attributed to the intensified etching and removal of surface functional groups. This is due to higher-energy collisions and an enhanced radical flux associated with higher plasma power conditions [22]. Consequently, the polar component of surface energy does not increase anymore, leading to a constant value of surface energy [14].

The observed fluctuation in surface energy of these polymers, characterized by an initial increase and then a rather constant amount of surface energy with higher plasma time and power, can be explained by complex surface reactions induced by ion bombardment, radical flux, and chemical modification. Initially, the higher-energy ions and radicals cause polar components of the surface which leads to increasing the surface energy. However, with further increases in plasma power, there might be an intensified etching and removal of surface functional groups, resulting in a constant surface energy [19]. A similar pattern is observed when increasing plasma time at a constant power, and likewise when increasing plasma power at a constant time. The accumulation of chemically active species on the surface enhances functionalization and polar interactions, causing an increase in surface energy. However, prolonged exposure to the plasma environment can lead to excessive surface etching and chain scission, resulting in the removal of surface functional groups and a constant surface energy [19]. The continuous interaction with plasma species over time leads to the formation of polar functional groups, enhancing surface wettability and interactions with polar liquids, ultimately increasing surface energy [23] up to a certain level where the removal of surface functional groups happen [19].

In summary, the variations in surface energy of these polymers, initially increasing and then remain constant with plasma power and time, highlight a delicate balance between surface etching and functionalization. This behavior can be advantageous when modifying polymer surfaces for specific applications requiring a combination of improved wettability and controlled degradation. These findings demonstrate the versatility of each polymer film

for various technical and industrial applications, providing valuable insights into their potential benefits and uses the following plasma treatment.

As mentioned previously, the surface tension was measured according to the Zisman model, where the contact angle (θ) is 0° . In this condition, the surface tension of the liquid equals the surface energy of the substrate. Therefore, based on the fact that we already know the surface energy of the substrate exactly after plasma treatment, if we observe a liquid with a contact angle of $\theta = 0^\circ$, it indicates that the surface tension is equivalent to the surface energy. In the Zisman model, the contact angle is indeed measured as 0° , indicating complete wetting of the liquid on the substrate. However, while it's true that the surface tension of the liquid equals the surface energy of the substrate in this idealized scenario, it doesn't necessarily mean that the surface energy and surface tension are numerically equal.

Surface tension refers to the energy required to increase the surface area of a liquid, while surface energy refers to the energy required to create a unit area of a particular surface. While they are related, they are not always numerically equal. In accordance with this model, for the sake of simplification, surface tension and surface energy are treated as equal, which holds true to some extent.

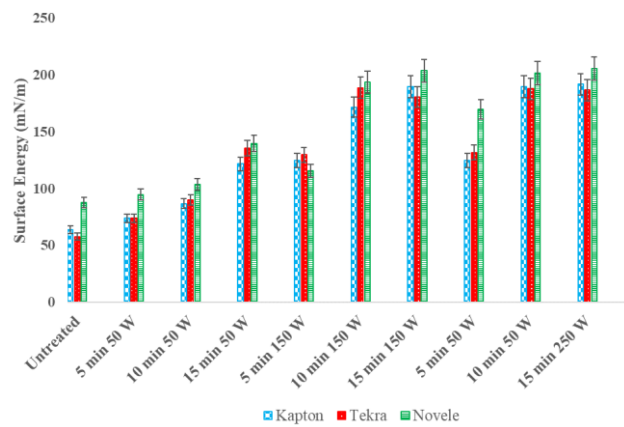
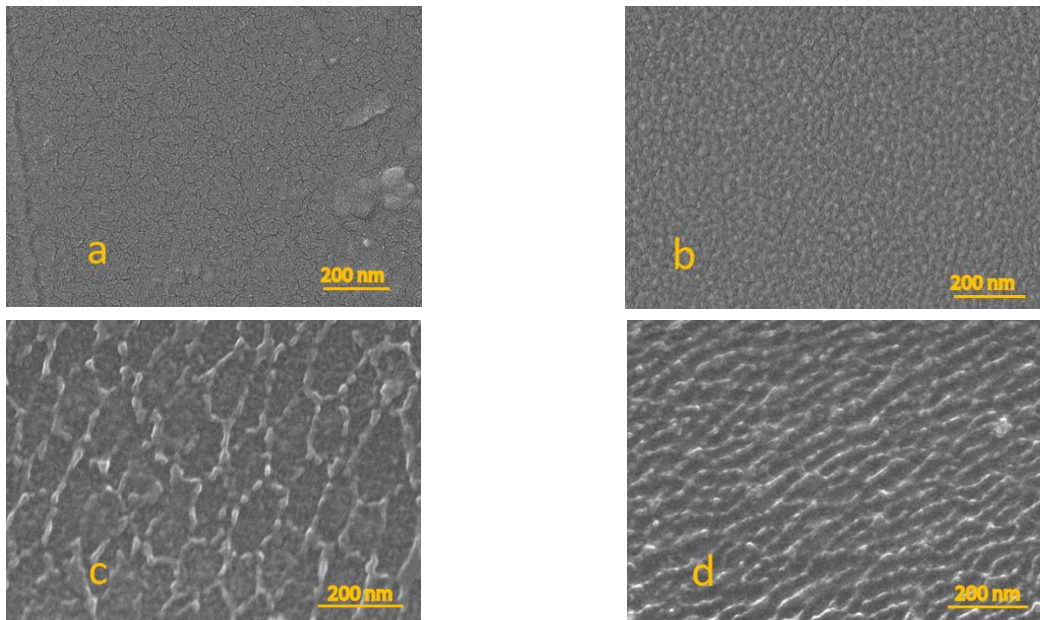


Fig 1 Variation of surface energy (mN/m) with a different time and voltage applied for plasma treatment.



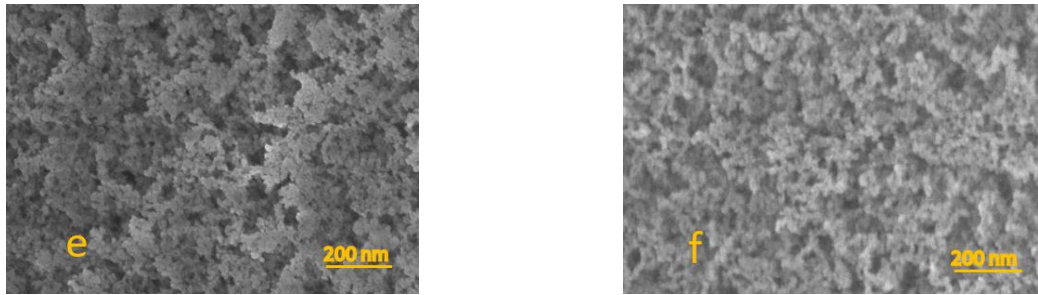


Fig 2 SEM images of the a) Kapton Polyimide before plasma treatment, b) Kapton Polyimide after plasma treatment c) Tekra PET before plasma treatment, d) Tekra PET after plasma treatment e) Novele (Ceramic coated PET) before plasma treatment, f) Novele (Ceramic coated PET) after plasma treatment; applying 15 minutes 250 W plasma treatment.

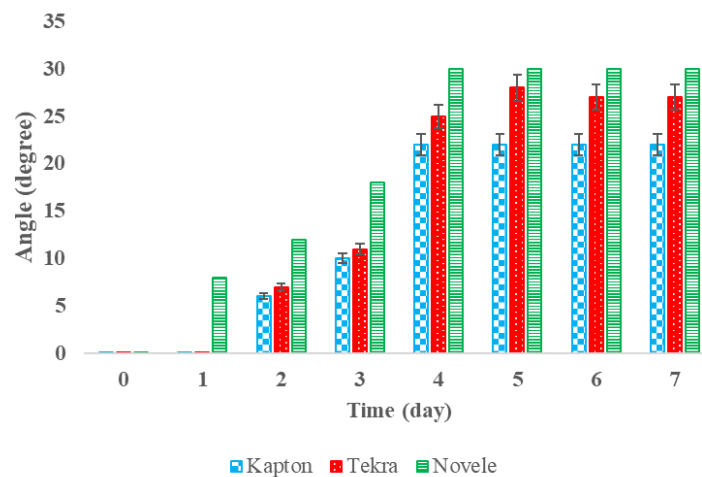


Fig 3 The contact angle of Kapton, Tekra and Novele substrates and silver ink on different days

V. CONCLUSION

This study has provided a comprehensive analysis of the surface energy properties of three widely used polymer films: Kapton polyimide, Tekra PET, and Novele (Ceramic coated PET). By employing contact angle measurements with DI water and ethylene glycol, we successfully characterized the surface energy of each polymer and investigated the effects of plasma treatment on these properties.

The findings highlight the importance of optimizing plasma treatment parameters to achieve the desired surface energy without compromising the material's integrity. The interplay between functionalization and degradation suggests that there is a critical threshold for plasma exposure, beyond which no significant benefits in surface energy can be obtained.

The results demonstrated that plasma treatment significantly modifies the surface energy of these polymer films by introducing polar functional groups, which enhance wettability and interactions with polar liquids. This enhancement is critical for applications requiring improved adhesion, such as in the fields of printed electronics, packaging, and graphic arts. Notably, the study found that while initial plasma treatment increases the surface energy of the substrates, further increases in plasma power and treatment duration lead to a stabilization of surface energy levels. This phenomenon is attributed to a balance between the functionalization of the surface and potential surface degradation due to extended exposure to plasma.

Specifically, our analysis showed that Kapton Polyimide exhibits excellent thermal stability and mechanical strength, with plasma treatment effectively enhancing its surface energy and wettability, making it suitable for high-performance applications in harsh environments, including aerospace and electronics. Tekra PET, known for its transparency and dimensional stability, saw improvements in surface energy due to plasma treatment, which is beneficial for its use in packaging and labelling where printability and barrier properties are crucial. Novele (ceramic coated PET) has an enhanced electrical conductivity due to its ceramic coating, making it ideal for flexible

electronics and printed circuitry, and plasma treatment further increased its surface energy, supporting its use in advanced electronic applications.

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