

# Exploring the Use of Nanoparticles to Modify the Surface Energy of Polyethylene (PE) Substrates

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## Abstract

In the plastics, packaging, and printing industries, it is generally known that printing on polyethylene (PE) substrates can be very difficult and often results in poor quality printing jobs. This phenomenon has been attributed to the low surface energy of PE substrates (~30-32 dynes/cm) relative to that of the printing inks. To improve the surface energy of PE substrates, flame, corona, plasma treatments are traditionally used to modify their surface energy, and in some instances, inorganic additives such as talc are also used to modify the surface energy of PE substrates. In the studies that have used inorganic additives to improve the surface energy of PE films, the researchers have observed that the smaller the particle size of the additives, the greater the improvements in the PE substrate's surface energy. While the particle sizes used in those studies were in the micron range ( $\mu\text{m}$  or  $10^{-6}$  meter), in this work the authors are using clay and graphene oxide nanoparticles (nm or  $10^{-9}$  meter) to modify surface energy of PE substrates and improve their printability. This novel process of modifying surface energy of PE films offers the following advantages: (1) the use of nanoparticles reduces the need for secondary processes such as flame, corona, and plasma treatments, and (2) improves the tensile strength of the PE substrates.

The preliminary results of this work show a slight improvement in the surface energy of PE substrates with clay nanoparticles. However, ongoing work with graphene oxide nanoparticles is expected to yield greater improvements because of its chemical composition.

## Introduction

Polymers such as polyethylene (PE) and polypropylene (PP) are used in packaging applications because these materials are inexpensive when compared to paper, metal, or glass. Also, they are easier to work with and use less energy to process. Figures 1 & 2 show examples of PE and PP packaging applications. Despite the advantages that polymers have over other materials in packaging applications, it is generally known<sup>3,4,5,6,7</sup> that some commercial polymers are difficult substrate to print on or to place labels on because of their low surface energy.



Figure 1. A PE milk jug.<sup>1</sup>



Figure 2. A PP packaging.<sup>2</sup>

To enhance the ability to print on these materials, their surface energy are increased using treatment such as corona treatment, Figures 3 & 4, plasma treatment, and flame treatment, Figures 5 & 6. Other methods that have used to improve the surface energy of these materials



Figure 3. Corona Treatment.<sup>8</sup>

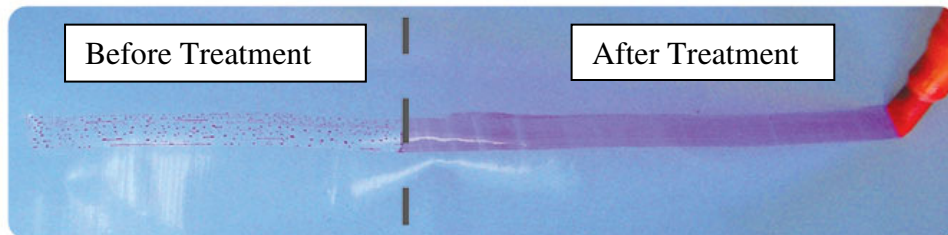


Figure 4. Corona Treatment.<sup>9</sup>

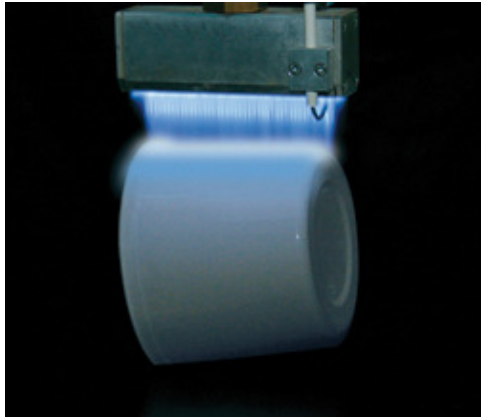


Figure 5. Flame Treatment.<sup>10</sup>



Figure 6. Labels placed after treatment.<sup>11</sup>

include coatings,<sup>4</sup> surface control additives,<sup>12</sup> which are used to lower the surface tension of the printing inks, and additives,<sup>3,13,14</sup> which are added to the polymers (substrate) to increase their surface energy. With regard to additives that are added to polymers for improving their surface energy, Ruiz<sup>7</sup> observed that the addition of 20 wt% of 1 $\mu$ m APS (average particle size) of calcium carbonate to LLDPE films raised their surface energy from 32 dynes/cm<sup>2</sup> (3.2 N/m<sup>2</sup>) to 38 dynes/cm<sup>2</sup> (3.8 N/m<sup>2</sup>). Arina, Honkanen and Tammela<sup>14</sup> working with talc, mica, and clay observed that these additives increased the surface energy (hence, printability) of polyethylene (PE) films. Furthermore, they observed that the surface energy of PE films increased from 32 mN/m to 37 mN/m with increasing additive content from 0 to 57 wt% and decreasing additive particle size. The particle sizes of the additives ranged from 1  $\mu$ m to 74  $\mu$ m. In this study, the authors have chosen to examine the effects of particle size and weight percent (wt%) content of additives on surface energy of polyethylene films. The commercial additives used in this study were Cloisite 20A nanoparticles by Southern Clay Products, Titanium dioxide, TiO<sub>2</sub>, nanoparticles, and microspheres by 3M.

## Theory

The mechanisms by which corona, plasma, and flame treatments increase the surface energy of the polymer substrates are not well known.<sup>15,16</sup> It has been proposed that these treatments “roughens the substrate surface, which provides sites for mechanical interlocking, and introduces reactive sites on the polymer’s surface (see Figure 7), consequently increasing the wettability and reactivity of the surface.”<sup>15</sup> The functionalities suspected to be introduced to the polymer’s surface include carbonyl, hydroxyl, hydroperoxide, aldehyde, ether, ester, and carboxylic acid groups. The mechanism of how the addition of additives increases the surface energy of polymer substrate is not well understood as well, but could be similar to the mechanism described above for corona, plasma, and flame treatment. It is suspected that polar nature of the carbonyl group of calcium carbonate and of the oxygen of TiO<sub>2</sub> increase the wettability of the polymer substrate.

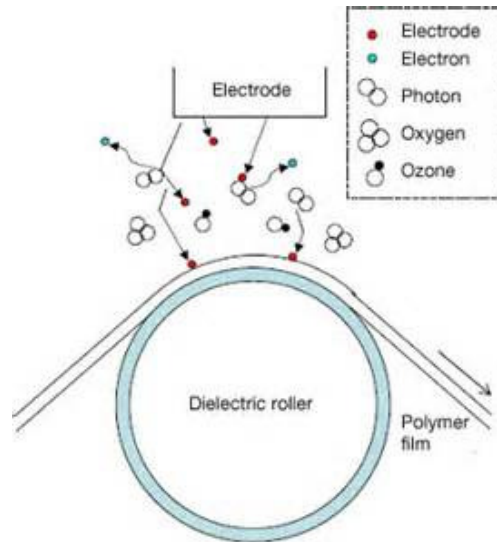


Figure 7. Corona Treatment of Polymer Substrate.<sup>17</sup>

### ***Substrate Wetting or Wettability***

Substrate wetting is defined as the replacement of adherent air at the substrate surface by a liquid coating or ink material.<sup>12</sup> Without good wetting, it is very difficult to achieve good quality printing. Consequently, it is important to determine substrates that have good wetting property. This is done by measuring the contact of a liquid drop placed on a substrate under static conditions. Good wetting occurs when the contact angle less than 90° and small as shown in Figure 8. Good wetting also equates to a substrate having relative high surface energy.

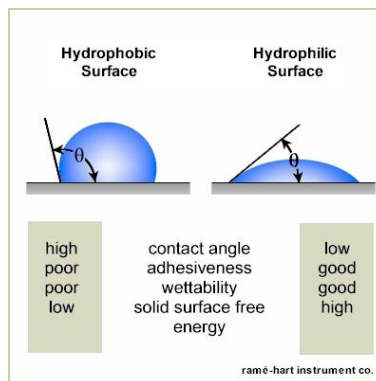


Figure 8. Contact Angle Measurement.<sup>18</sup>

### **Experimental**

**Materials:** High density polyethylene (HDPE), Sclair® 19C by NOVA Chemicals was used as the substrate in this work. This polymer was described by the manufacturer as a film extrusion grade HDPE with a melf flow index of 0.95 g/10 min at 190 °C/2.16 kg.

**Additives:** The additives used in this study include Cloisite® 20A nanoparticles by Southern Clay Products. These particles were natural montmorillonite clay modified with a quaternary ammonium salt. Cloisite® Na+ nanoparticles were also used in an attempt to increase the presence of polar groups at the substrate surface. 3009 and 3029 HDPE/Maleic Anhydride Polybond® by Chemtura Corporation were used to promote the bonding of the nanoparticles to the HDPE substrate.

Other additives used were TiO<sub>2</sub> nanoparticles and ceramic & glass microspheres by 3M.

**Procedure:** A paint shaker was used to mix the formulation of HDPE, nanoparticles, and polybond in a gallon paint can before introducing it into a Brabender counter-rotating twin screw extruder. The extrudates from the extruder were pelletized and introduced into a Brabender blown film extruder with a mini-tower. The surface energy of the blown films produced were measured using Tantec model CAM-MICRO contact angle measuring instrument.

## Results

**Table I. Contact Angle Measurement**

Material (wt%)	Contact Angle	Surface Energy (dynes/cm)	Difference (dynes/cm)
HDPE	81±12	34.4	---
HDPE/PB (80/20)	87±17	30.3	(-4.1)
HDPE/PB/Cly (80/10/10)	72.4±4.8	39.7	5.3
A125 (82.5/8.8/8.8)	87±13	30.4	(-4.0)
B250 (85/7.5/7.5)	82.4±3.5	33.4	(-1.0)

Table I shows the preliminary results of this work. It showed that the formulation of 80/10/10 wt% of HDPE/Polybond (PB) /Cloisite ® 20A (Clay) increased the surface energy of HDPE by about 5.3 dynes/cm (0.53 N/m). Other formulations showed a decrease in the surface energy of HDPE. Of particular interest are the A125 and B250 formulations, which contained the Cloisite® Na+ nanoparticles at the following wt%: A125 had 82.5/8.8/8.8 wt% of HDPE/PB/Cloisite® Na+, while B250 had 85/7.5/7.5 wt% of HDPE/PB/Cloisite® Na+. These formulations decreased the surface energy of HDPE films, which suggests, as described in the theory section, that polar groups containing oxygen, such as the carbonyl or hydroxyl, are the preferred polar groups for increasing the surface energy of PE films.

The authors are presently working with other additives and plan to present their findings in the final draft of this paper.

## Conclusion

Preliminary results showed that the use of nanoparticles to increase the surface energy of HDPE films was successful with a formulation containing 80/10/10 wt% of HDPE, PB, and Cloisite® 20A (Clay nanoparticles). The results also showed that the use of nanoparticles containing Na<sup>+</sup> do not increase the surface energy of HDPE films. The authors would like to remark that this is an ongoing study in which other nanoparticles are also being examined. The authors are using graphene oxide nanoparticles as a means of introducing oxygen polar group to the polymer substrate as suggested by several authors.<sup>15-17</sup> The results of these findings will be presented at the conference.

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### **Biographies**

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