Preparation and characterization of CO₂ plasma treated polypropylene grafting with soybean oil

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Abstract. In this study, the adhesive properties of the CO₂ plasma modified polypropylene (PP) surfaces have been investigated. The proportion of soybean oil would affect the grafting rate. The grafting rate increased with the increasing of the proportion of soybean oil. The grafting rate decreased when the proportion of soybean oil beyond 50%.

1. Introduction
Polymeric materials like polypropylene (PP) were used in fabrication of secondary structures of aircraft, automobiles, railway coaches, civil construction as well as biomedical application due to their superior properties like better corrosion resistance, high strength to weight ratio, relatively low cost and easy recycling. However, polypropylene is a hydrophobic polymer due to its nonpolar hydrocarbon part, and the poor adhesion is expected between a hydrophilic coating and PP substrate. Surface modification of polypropylene (PP) materials is the essential step to achieve the desired surface chemistry, roughness or compatibility with biological systems. Surface modification techniques which can transform polymers into highly valuable finished products have become an important part of the plastic technologies [1-4].

Several surface modification methods are employed to modify the polymer surfaces, such as chemical, thermal, mechanical and electrical treatments [5-7]. Recently, research on the use of plasma treatments has grown in interest. Plasma treatment is an appropriate method. Plasma treatment is a dry, fast and environmentally friendly technique. Plasma treatment of polymers, including corona discharges, is now widely used industrial technique to modify surfaces of many different materials (metals, semiconductors, polymers, and ceramics). Polymers are often modified using rare gas (He, Ne, and Ar), reactive gas (O₂ and F₂) plasma [8-13].

Surface modification of polymers with low-pressure plasma has gained great scientific and industrial importance and it is often used to improve adhesion of coatings, wettability, printability, biocompatibility and other surface related properties of polymers [14].

Results showed the formation of polar groups such as C=O and OH in the PP surface following the plasma treatment[15]. The DBD plasma treatment insignificantly affected the mechanical properties of the PP film [16].

In this study, the adhesive properties of the CO₂ plasma modified polypropylene (PP) surfaces have been investigated. The grafting of PP was analyzed by FTIR, SEM.
2. Experimental procedures

2.1. Materials
Polypropylene (PP), ipp1701, Sinopec yanshan petrochemical company. Soybean oil, AR, Aladdin industrial corporation. Xylene, AR, Keruisi corporation, Tianjin.

2.2. Procedure for plasma grafting of PP
The plasma equipment was used to carry out the CO₂ plasma treatment. The gas was injected for 2min to remove the air in the device before experiment. Then PP was put into the device. The flow of gas was 40–60ml/min. The voltage and the electric current was 40V, 2A. PP was discharged for 10min. Then, the sample was placed for 5min in the air.

2.3. Soybean oil grafted PP
The soybean oil was dissolved in xylene. And the PP after treatment was throw into the solution of soybean oil and xylene for 4h in 135°C. The polymerization products were washing three times by ethanol after cooling. The remaining soybean oil and solvent on the products was removed by vacuum pump. Then the samples were washing in the thermostatic magnetic stirrer for 24h. The liquid was filtered out by vacuum pump and then put into an incubator to dry for 24h before being weighed.

3. Surface characterization techniques

3.1 The grafting rate
In this experiment, the grafting rate (GD) of PP was determined by weighing method. The formula is as follow:

\[
GD = \frac{(M_g - M_0)}{M_0} \times 100\%
\]

\( M_g, M_0 \) was the weight of PP after/before grafting.

The grafting rate of PP with different proportion of soybean oil and xylene was list in table 1.

| Table 1 The grafting rate with different proportion of soybean oil and xylene |
|-------------------|---|---|---|---|
| The proportion of soybean oil (%) | PP (g) | Xylene (ml) | Soybean oil (ml) | Grafting rate (%) |
| 100 | 3.00 | 0 | 16 | 1.15 |
| 75 | 3.00 | 4 | 12 | 3 |
| 50 | 3.00 | 8 | 8 | 5.2 |
| 25 | 3.00 | 12 | 4 | 1.5 |

There was no solvent in the system when the proportion of soybean oil was 100%. The grafting polymerization could be initiated but with low rate, which indicated xylene would affect the grafting rate. Xylene dissolves long-chain unsaturated fatty acid and disperses them in solvents instead of aggregating, making it easier to form macromolecular free radicals, and then macromolecular free radicals can be grafted onto PP. The grafting rate is up to 5.2% while the proportion of soybean oil was 50%. The soybean oil was dispersed in xylene easily once the proportion of xylene exceeds 50%. But a large amount of xylene would etch the amorphous of PP at high temperature, and the crystalline region of PP was arranged tightly and couldn’t graft the soybean oil. Therefore, The grafting rate decreased to 1.5%.

3.2 FTIR
The FTIR spectrum of PP with different grafting rates was shown in figure 1. The FTIR spectrum showed the peaks in the range of 3000 cm⁻¹–2800 cm⁻¹ and in the peaks 2956 cm⁻¹ and 2872 cm⁻¹ the CH₃ symmetric and the asymmetric stretching vibrations can be attributed. The CH₂ symmetric and asymmetric stretching vibrations showed the peaks range at 2920 cm⁻¹ and 2842 cm⁻¹. The
bending vibration of CH₃ and CH₂ were showed in 1400 cm⁻¹. The soybean oil grafting PP induced by plasma treatment showed C=O absorption peak at 1750 cm⁻¹ compared with pure PP. The absorption peak of C=O is obvious when the proportion of soybean oil is 50% and the grafting rate is 5.2%. The peak in 1260 cm⁻¹ and 1300 cm⁻¹ could be seen from figure 1 and figure 2, which belong to −OH and C=O of carboxylic acid, and indicated that the soybean oil have grafted with PP.

![Figure 1](image1.png)

**Figure 1** The FTIR spectrum of PP with different grafting rates

![Figure 2](image2.png)

**Figure 2** The FTIR spectrum of soybean oil

### 3.3 SEM

The morphology of PP with different condition was shown in figure 3. It can be seen that the surface of PP without treatment is smooth relatively figure 3 (a). The surface of PP after the treatment of CO₂ plasma had a certain degree of etching, because of the high energy particles of plasma could etch the amorphous areas of PP figure 3 (b). The grafting rate of PP was low to 1.15% when the proportion of soybean oil was 100%. The graft layer on the surface of PP is loose relatively and the cavity on the surface of PP is the result of plasma etching figure 3 (c). The grafting particles on figure 3 (d) (the
The grafting rate was 5.2% (a) (the grafting rate was 3%), and not obviously. That may be introduced by the high grafting rate that cause the grafting layer became dense. The etching on the surface of PP by xylene was more seriously when the proportion of soybean oil was 25%. It can be seen from the figure 3(f), the amorphous area on the surface of PP was etched away.

Figure 3 the morphology of PP graft soybean by plasma

(a) untreated PP  (b) the morphology of PP etched by CO₂ plasma

(c) the proportion of soybean oil 100%  (d) the proportion of soybean oil 75%

(e) the proportion of soybean oil 50%  (f) the proportion of soybean oil 25%
4. Results
It could be seen from FTIR and SEM, CO$_2$ plasma could induce the grafting of soybean oil on PP, the proportion of soybean oil would affect the grafting rate. The grafting rate increased with increasing of the proportion of soybean oil, the grafting rate decreased when the proportion of soybean oil beyond 50%. There were two reasons for that: 1. The energy of the plasma couldn’t break bonds indefinitely. 2. Xylene etched the amorphous region of PP, and the crystalline region of PP couldn’t graft the soybean oil.

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