

## Material Properties

## Enhanced adhesion of polypropylene to copper substrates



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## ABSTRACT

Varying concentrations of maleic anhydride (MAH) were grafted onto three types of polypropylene (PP) in the presence of dicumyl peroxide (DCP). Pull-off adhesive strength from a copper substrate, tensile Young's modulus, and tensile strain-at-break were determined and SEM observations made as a function of the MAH concentration for each PP. One of the PPs plus 3 wt% MAH provides a high value of the adhesive strength along with the Young modulus and the strain-at-break sufficient for the use as a coating for copper wires and cables.

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## 1. Introduction

Polypropylene (PP) is a polyolefin thermoplastic valued for its ease of processing, mechanical toughness, low cost, flexibility, electrical resistivity, and resistance to chemical degradation and wear [1–3]. These properties have made PP useful in applications such as construction, automotive parts, aircraft components, biomedical equipment, packaging, clothing, roofing, loudspeaker drive units, among others [1,4].

Polypropylene's properties also make it an excellent candidate for polymeric coatings. For instance, polypropylene could be applied to metals as insulation in electrical wiring, or as a membrane to mitigate corrosion and wear of the metal surface. However, due to its low surface energy, polypropylene lacks sufficient adhesion to metal substrates. There are some established methods of improving the interfacial adhesion of polypropylene, such as flame treatment or corona treatment [5–7] but these methods often weaken thermally sensitive polymers, or are expensive to carry out, requiring sophisticated equipment which needs a significant amount of energy to maintain.

Thus, the worthwhile task we see is the development of PP coatings on metals such as copper, taking particular care of sufficient adhesion between the constituents. Our task can be considered 'an inverse' of that undertaken by Ramsteiner and coworkers who have created hard coatings to increase the scratch resistance of polymers [8]. While the coating scratch resistance is desirable for us also, hard films can undergo embrittlement [8]. In a way, our task is easier: we would like to get flexible coatings on relatively flexible (sometimes thin) copper wires. While in some cases the speed of coating deposition is important [9], this is not a primary factor here. In contrast to situations when the electric resistivity of the polymer has to be lowered [10], we need a coating with high electric resistivity.

Our literature survey led us also to a process outlined by Gaylord and Mishra [11]. Maleic anhydride (MAH), a plasticizer commonly used for the manufacture of unsaturated polyester resins [12], is grafted onto the PP chains in the presence of organic peroxides. The mechanism of this reaction is still under debate, but has been tentatively explained by Dean et al. [13]. The organic peroxide acts as an initiator for the grafting reaction. Splitting along the oxygen-oxygen bond of the peroxide generates a free radical. In turn, this radical induces yet another radical at the tertiary carbon of the polypropylene molecule. After these steps, two things can occur: the polymer can either accept an MAH molecule directly, or undergo scission along the carbon-carbon bond before the MAH is grafted to its structure. In either case, an MAH graft-copolymer

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**Table 1**  
General physical and mechanical properties of polymers.

Polymer	Density (g/cm <sup>3</sup> )	Melt Flow Rate (g/10 min)	Tensile Strength at Yield (MPa)
PP1	0.9	35	21
PP2	0.9	2.6	22
PP3	0.9	20	24

(MAPP) is created. MAPP has traditionally been used as a coupling agent to improve the homogeneity of polymer composites with organic bio-flours or other polar materials 14–16. We have decided to try to utilize MAH to promote adhesion of polypropylene to metallic surfaces. We have used several various grades of polypropylene and determined the effect of MAH concentration on the adhesive and mechanical properties of those polypropylenes.

## 2. Experimental

### 2.1. Materials

Three types of polypropylene—code named PP1, PP2, and PP3—were used. PP1 was provided by Exxon Mobil, PP2 was obtained from LyondellBasell while PP3 was obtained from PolyOne (see Table 1).

The peroxide initiator used was dicumyl peroxide (DCP). DCP and MAH were purchased from Sigma-Aldrich Chemical Co. The 1/16th inch thick copper sheets used for adhesion testing were made by Speedy Metals Company in Frasier, Michigan.

### 2.2. Sample preparation

Twelve different MAPP copolymers were tested. For each of the three types of polypropylene, four samples of varying MAH concentration were prepared: 100% polypropylene with no MAH or DCP added, then in turn 3 wt%, 6 wt% or 8 wt% MAH. All samples in which MAH was added contained an additional amount of DCP that

constituted 1 wt % of the sum of both the polypropylene and the MAH in each sample.

The grafting process was carried out under conditions defined in a previous study by Agjeh et al. [17] and apparently found effective. While these authors have performed grafting of a polyethylene, we found their procedure—including the use of MAH together with DCP—applicable well to our polypropylenes. Copolymers were created in a Brabender type 6 twin-screw mixer at 60 RPM and 190 °C. First, polypropylene and MAH were placed in the mixer; then after 2 min the DCP initiator was added and the reactants were mixed for additional 4 min. Aghjeh and coworkers reported that the feeding order is important for successful grafting [17]. They have also reported that low rotor speeds lead to lower grafting yields.

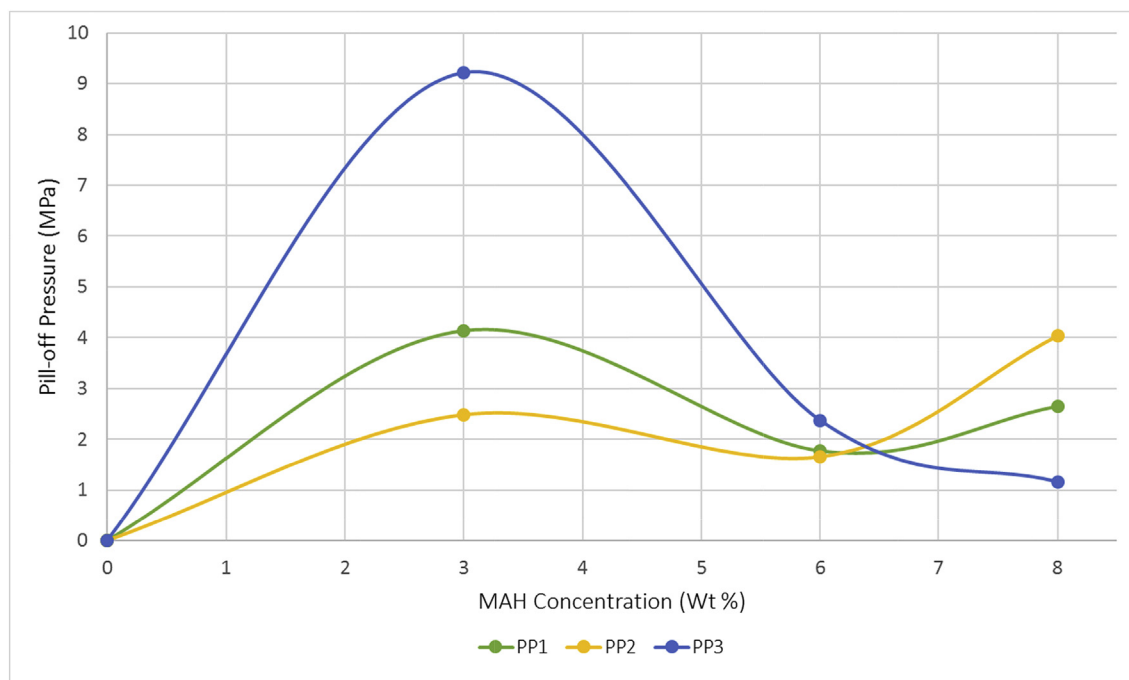
Each MAPP sample was then pulverized in a milling machine (model LC-124 from the Gilson Company, Inc.) and then compression molded using a hydraulic press in one of two ways. One set of samples was pressed onto the copper sheets at a temperature of 190 °C and a pressure of 0.01 MPa for 10 min. Another set of samples used for testing of tensile testing and tribology were pressed into molds at 190° C and 0.12 MPa for a period of 20 min.

### 2.3. Adhesion testing

Adhesive strength for each polymer coating was determined using an ASTM D4541 standard pull-off test. A DeFelsko PosiTest adhesion tester was used. Circular metal dollies, 14 mm in diameter, were glued to the coated sheet using cyanoacrylate super-glue and left to cure for 24 h. After the curing period, a hydraulic actuator is placed over the dollies and the pressure required to remove the coating from its substrate is recorded. Four values were taken and averaged for each copolymer.

### 2.4. Tensile testing for Young's modulus and strain-at-break

Tensile testing (in accordance with the ASTM D638 standard) was performed using an Instron universal testing machine. Two



**Fig. 1.** Effect of MAH on adhesion strength of polypropylenes to copper sheets.

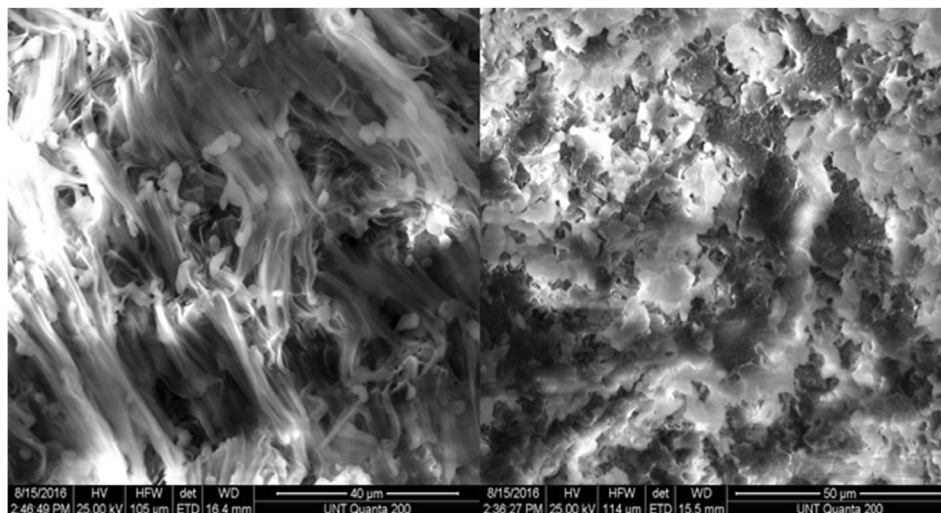


Fig. 2. Scanning electron microscopy images of neat polypropylene (left) and MAH-grafted polypropylene (right).

steel grips hold a dog-bone-shaped sample and pull it apart until fracture. The machine measures the force applied, the cross-sectional area of the sample is known, the sample elongation is measured and the tensile Young modulus calculated. Averages from four tests were calculated for each composition.

### 3. Adhesion

The results are displayed in Fig. 1.

Fig. 1 tells us that grafting MAH onto all three types of polypropylene provides adhesion—where was none before. All pure polypropylene samples simply did not adhere to the sheets and therefore could not be tested. At concentrations up to 6 wt% MAH, PP3 exhibits an adhesive strength significantly higher than those of PP1 and PP2. In general, the adhesive strength of the samples peaks at a concentration of 3% by weight, and after more of the coupling agent is added, the adhesive strength decreases. This weakening of

the bond can again be explained by the mechanism for the grafting reaction proposed in Ref. [11]. Aside from causing the carbon-carbon scission of the polymer chains, the free radicals generated by DCP can also allow MAH to attach to the free oxygen from the split peroxide. At low concentrations of MAH, there are enough DCP molecules to generate radicals on the polymer molecule for the MAH to attach itself to. However, for a given concentration of DCP and an increasing concentration of MAH, the alternative reaction takes over, and less of the coupling agent is grafted to the polymer.

### 4. SEM results

The above results can also be explained by SEM images taken of non-grafted and grafted samples of polypropylene; see Fig. 2.

The chain structure of the polymer is more clearly visible in pure polypropylene (left) than in MAPP. During the grafting process, the peroxide-initiated scission of polypropylene molecules along their

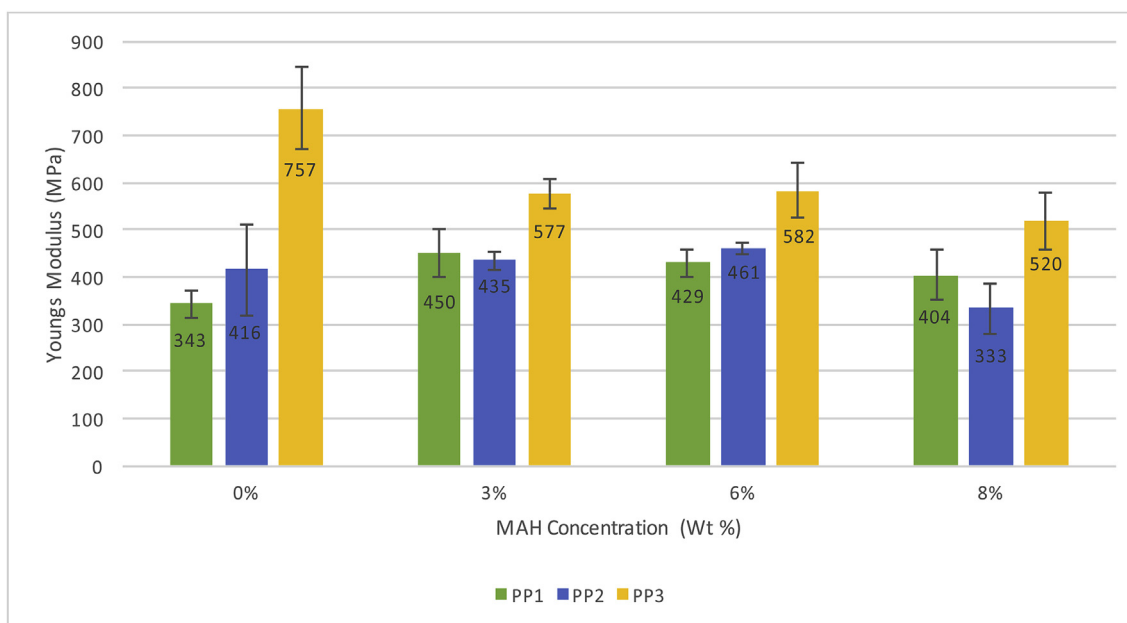


Fig. 3. Effect of MAH concentration on tensile Young's modulus.

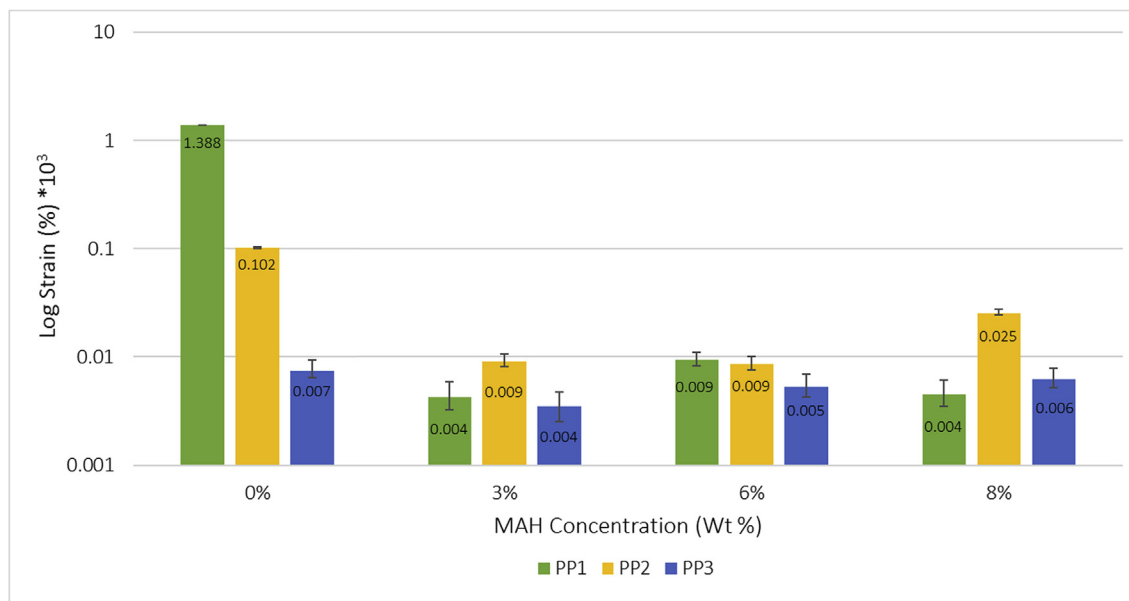


Fig. 4. Effect of MAH concentration on tensile strain-at-break.

tertiary carbons shortens the chains of the polymer. The chain shortening is expected to result in a more brittle material—a prediction that will be verified in the next Section.

## 5. Tensile testing results

Results for Young's modulus and strain-at break are shown in Figs. 3 and 4 respectively.

In PP3 samples, the addition of MAH reduces the Young modulus, but this reduction does not vary significantly with the concentration of MAH in the copolymer. In PP1 samples, the modulus is higher than for the sample without MAH, but changes little in the range of MAH concentration from 3 to 8 wt%. In PP2 samples, the modulus changes little in MAH concentration range from 0 to 6%, but decreases for 8% MAH.

The strain-at-break for all three types of polypropylene is severely reduced by MAH grafting for PP1 and PP2. The strain at break is fairly low for PP3 without MAH, becomes still lower at 3% MAH, but then increases with adding more MAH. We recall that the strain-at-break  $\epsilon_b$  is inversely proportional to brittleness B [18,19].

## 6. Conclusions and final comments

The key property for us is adhesion of polypropylene to copper since we are dealing with application of the polymer for copper wires and cables. The best results are seen for PP3 containing 3 wt% MAH. The tensile Young modulus for this composition is quite acceptable. The strain at break  $\epsilon_b = 3.51\%$  is acceptable also since coatings for wires and cables are subject to stresses far from the point of fracture.

Not mentioned above is the fact that the coating cooling rates are important. Low cooling rates affect adversely the adhesion.

In earlier work mild steel was coated by a polymer, namely by an epoxy [20]. The main requirements for the coating were low friction and low wear; these were achieved by inclusion of a fluoro-polymer and using in turn two curing agents. The present work in conjunction with [20] allows at least some comparisons of a thermoplastic coating on a metal vs. a thermoset coating on a metal. Application of thermoplastics as coatings is simpler in principle, a

curing agent and a curing stage of the operation not needed. At the same time, in terms of costs, thermosets are often somewhat cheaper.

As for friction and wear, the former is important when the polymer is used as a coating for high voltage (600 V) copper wires and cables. During installation for service, a wire or a cable can be moved more easily and using a lower force if the dynamic friction is lower. Once installed, low wear is not an important requirement.

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