

## Surface Modification of CSM Fibers Using Branched Additives

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**Project No. M04-CL11**

**Project Team:**

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**GOAL STATEMENT:**

The primary objective of this research is to modify the surfaces of polypropylene (PP) capillary surface material (CSM) fibers (Figure 1) through the use of migratory additives, i.e., material added to the melt that exhibits controlled migration to the surface of the fiber. The additives to be investigated include linear molecules as well as well-defined comb-like molecules with polyethylene backbones and highly regularly spaced pendant functional groups. Hyperbranched additives, with very different architectures, will also be studied for their surface-modifying effectiveness. The architecture of the comb and hyperbranched modifiers and the chemical identity of the pendant/terminal groups will be varied to examine the effect on the surface properties of the CSM fibers.

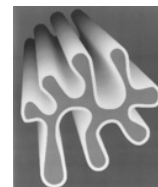


Figure 1. CSM Fiber

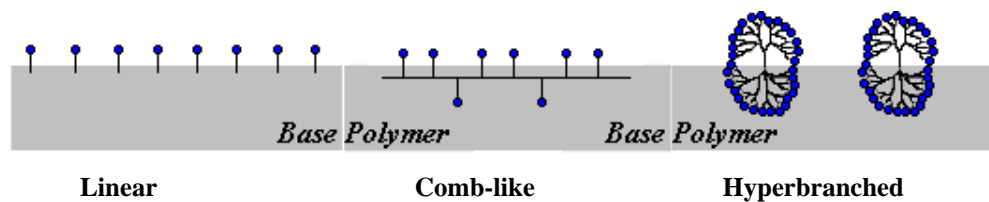
**ABSTRACT:**

Linear and branched hydrophilic additives of various molecular weights and functional group densities were added to PP as surface modifiers to make blend films through solution drop coating and heat pressing from melt-blended mixtures. Water contact angles on the film surfaces were measured over one week to investigate the additive migration behavior. In particular, PP-additive blend films made through melt blending exhibited lower water contact angles and more uniform distribution of additives on the film surfaces than those made through solution drop coating. A commercial product, Ciba® IRGASURF HL560, was selected as a reference to evaluate the effectiveness of proposed additives in generating hydrophilic surfaces. Linear polyethylene glycols (PEG) and multi-arm polyethylene oxides (PEO) were found to generate favorable wettability on the PP films, relative to the commercial product when the same weight percentage of additive was used, while hydroxyl-terminated dendritic polyesters were less

effective than the other additives.

## **INTRODUCTION:**

This research involves fundamental studies of polymer additives with novel architectures and their effect on the surface properties of CSM fibers. Relative to the surface energy of the base polymer, we intend to create hydrophilic surfaces for liquid transport and biomedical applications, as well as hydrophobic surfaces for applications where adhesion and release control are important. PP was selected as the base polymer as it has wide use as woven and non-woven fabrics for hygiene, medical, absorbent and filter applications [1, 2]. Methods to modify this naturally hydrophobic polymer can be classified into two categories. One is to change functionalities on the fiber surfaces through chemical reaction or treatment, e.g., photografting polyacrylamide onto the fiber surface as the fiber is subjected to UV light in the presence of photoinitiators [3] or incorporating polar function groups by exposure to plasma conditions [4, 5]. Another is to physically apply hydrophilic additives by topical coating with spin finishes [2]. However, fiber finishes are not durable on the surfaces. In the case of CSMs that contain axial grooves, a significant portion of the solvent may be trapped in the grooves due to the capillary pressure created by the small radii of curvature present in the cavities. As a means to overcome the permanence and coverage issues with solution-coating techniques, this research will investigate the surface modification of CSM fibers using migratory additives. Migration of functionalized additives dispersed in the base polymer to the surface has been recognized as a low cost and reliable method to generate durable specific surface properties [6, 7, 8]. In general, the ability of an additive to migrate to the surface is defined by several factors such as size, mobility, end-group functionalities, relative composition, and molecular architecture, among others. In addition, careful selection of additives with appropriate functionalities provides significant control over the hydrophobicity or hydrophilicity of the modified surface while retaining the bulk properties. In this regard, surface modification using linear as well as branched additives has been studied in the process of rendering polyolefinic surfaces hydrophobic or hydrophilic [9, 10, 11], however, a systematic correlation between the additive architecture and its migratory behavior has not been explored.



**Figure 2. Current and proposed additive technologies.**

In this study, we are investigating the effect of additive architecture and end group functionality on its migratory behavior to tailor the surface properties of the base polymer to desired specifications. The architectures to be explored in this study include linear, comb-like, and hyperbranched additives that are shown in Figure 2, each of which will be varied with respect to the block length and end group functionalities. In this report, water contact angles on blend films of PP with linear, multi-arm, and hyperbranched additives of various chain length and weight percentage will be presented. Effects of substrate, film making method, and aging time on additive migration will also be discussed.

#### **EXPERIMENTAL SECTION:**

*Materials.* Isotactic PP (Dow INSPIRE 112) was obtained from Dow Chemical Company as the base polymer for this study. Linear PEGs with molecular weights of 1000, 2000, and 10000 Da and four-arm hydroxyl-terminated PEOs with molecular weights of 2000, 10000 Da were purchased from Polymer Source Inc. and used as received. Xylene was purchased from Aldrich Chemical Company and used as received. Ciba® IRGASURF HL 560 of 40% PP pre-blended with 60% active additive was received from Ciba Specialty Chemicals as the reference. Dendritic polyester BOLTORN® H30 and H40 with 32 and 64 terminal hydroxyl groups were purchased from Perstorp Inc., chemical structures illustrated in [12].

*Preparation of PP-additive films through drop coating.* For this phase of the research, the PP was formed into films rather than fibers because films are easier to make in small quantities and they are more amenable to surface characterization. A mixture of PP (100 mg) and additive (5, 10 and 15 wt%) was dissolved in 10 ml xylene at 136 °C with continuous stirring by a magnetic bar and with reflux for 30 min under nitrogen. A few solution drops were dripped onto silicon and Teflon substrates. Circular films were formed by vaporizing the solvent in air at room temperature overnight. The average diameter of the films was 1.3 cm, and the thickness was 50 μm. Films were stored at ambient temperature until further characterization.

*Preparation of pp-films through heat pressing.* A mixture of PP (5 g) and 5 wt% additive was

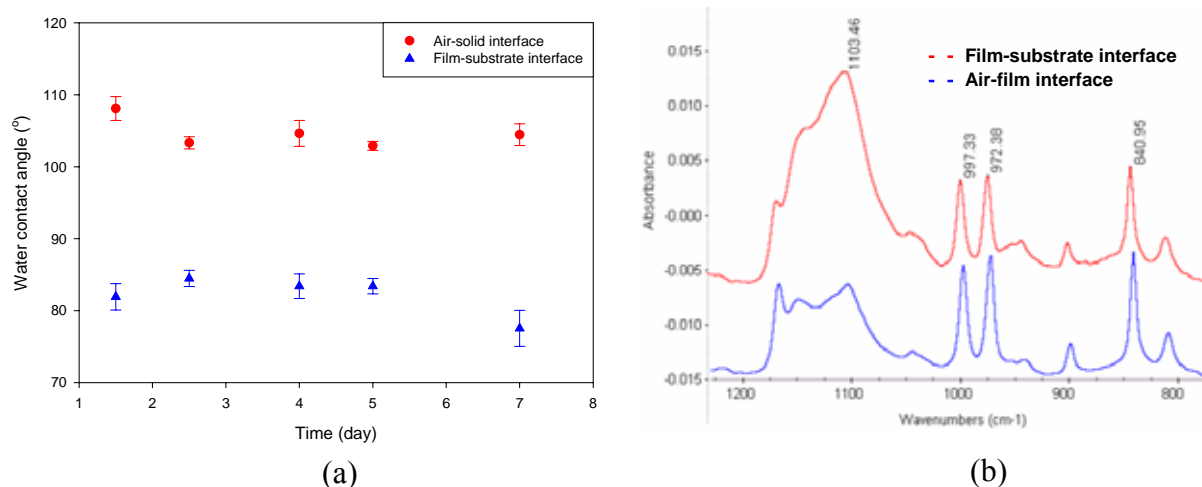
melt blended in a glass beaker and stirred with a spatula at 230 °C in a convection oven for 20 minutes. After the mixture cooled to room temperature, approximately 20 mg from the melt-blended mixture was then heat pressed at 230 °C between two glass slides to make films. The films had an average diameter of 1.3 cm and a thickness of 150  $\mu\text{m}$ . Films were stored at room temperature.

*Characterization.* Static water contact angles on the PP-additive blend films were measured *via* a sessile drop technique using a Kruss DSA10 goniometer equipped with a digital photo-analyzer. Analysis was carried out in a closed chamber with glass windows after the atmosphere was pre-equilibrated with water vapor at 30 °C for at least 3 hours. A similar procedure was discussed by Wong et al. [13]. Water drops of 0.5  $\mu\text{L}$  were placed onto a film surface and were allowed to equilibrate for 30 seconds before making a measurement. Water with a resistivity of 18 m $\Omega$  used in this study was obtained from a Millipore Milli-Q system. The contact angles were calculated using Kruss DSA10 drop shape analysis software and an average of at least 3 drops per specimen is reported.

## **RESULTS AND DISCUSSION:**

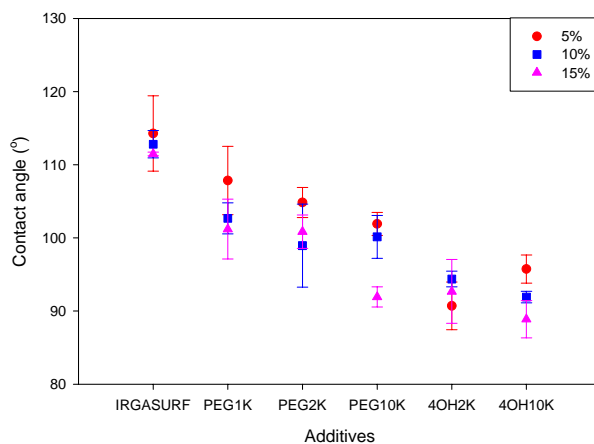
*Effect of interfacial energetics.* Some of the specially synthesized additives are available in only limited supply, so relatively small PP films incorporating each additive were formed in silicon or glass substrates. In the blend films, the hydrophilic additives are the components of high surface free energy and the base polymer PP has relatively low surface free energy. Polar additives are likely to migrate toward the high-energy interface on the silicon wafer side instead of to the air-solid interface, which has a low free energy. This is verified by the contact angle difference (Figure 3a) as well as the ATR-FTIR spectra (Figure 3b) on both sides of a film removed from a silicon substrate. The PP film containing 5 wt% four-arm PEO (2000) was made from drop coating onto silicon wafer. Contact angle on the film-substrate side had an average of 80°, lower than the air side, indicating that more additive migrated to the silicon substrate than to the air-film interface. ATR-FTIR spectra were consistent with the water contact angle data. On the substrate side, the FTIR spectrum showed a stronger C-O-C peak at 1100  $\text{cm}^{-1}$  than on the air side. By way of comparison, films were also formed on low energy Teflon substrates using 5wt% four-arm PEO (2000). The average air-film contact angle for the film on the silicon substrate was 110°, and that on the Teflon substrate was 90°, meaning that less additive migrated to the Teflon surface and was therefore available to improve the hydrophilicity

of the air-film surface.



**Figure 3. Effect of substrate (a) Contact angles on both sides of the film drop-coated on silicon wafer over one week. Films containing 5wt% four-arm PEO were stored at room temperature. (b) ATR-FTIR spectra of both sides of the same film.**

*Films made through drop coating on Teflon.* Circular films containing 5, 10 and 15 wt% additive were made through drop coating on Teflon. These films were 1.3 cm in diameter and 50 μm thick. Water contact angles were measured along the radial direction of the circular films, but only the measurements at the center of the film are reported here (Figure 4).



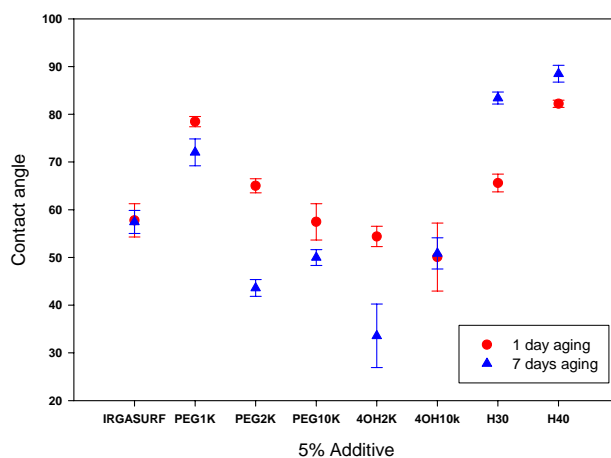
**Figure 4. Comparison study of contact angles on films made through drop coating on Teflon.**

In general, four-arm PEOs (2000, 10000) exhibited lower contact angles than linear PEGs (1000, 2000, 10000), likely due to the higher concentration of –OH groups in the four-arm PEOs.

However, films made through drop coating with selected additives did not show significantly improved hydrophilicity. The average contact angle for all additives was greater than 80°.

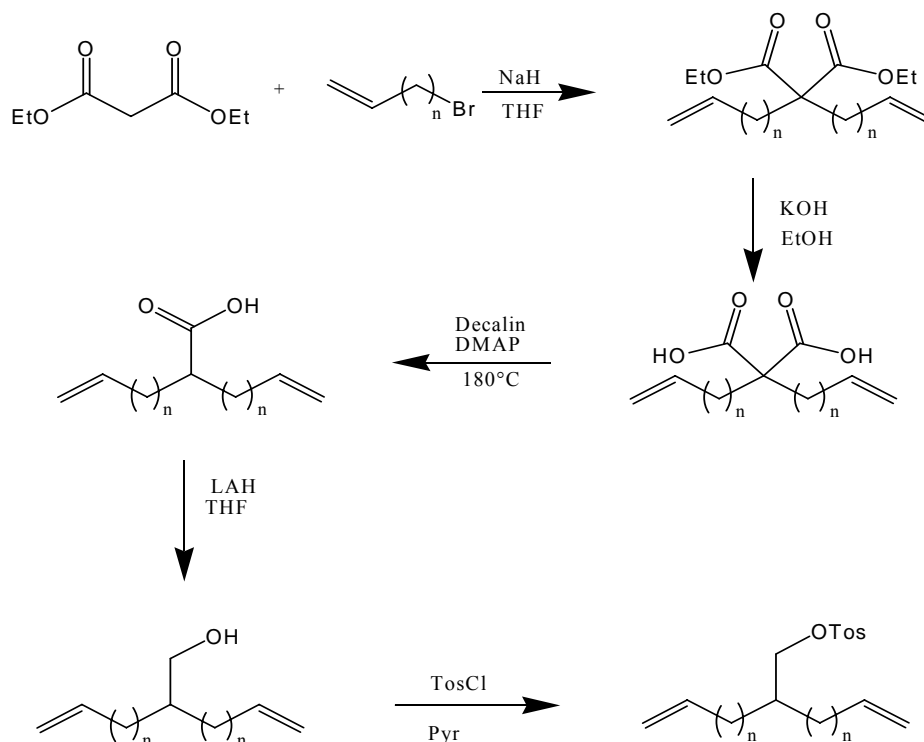
*Films made through heat pressing melt-blended mixtures.* Last year (and in the previous sections here) we presented a large amount of data from films that were formed from solution. However, PP CSM fibers are produced through melt extrusion, so our recent work has been done with melt blending. Since limited quantities of certain additives are available, small-scale blending was done in a beaker as discussed in the “Experimental Section.” Uniform mixing of additives into PP is an important issue for making polymer blends. It can be affected by temperature, mixing duration, and shear rate. PP and additives were melt blended for 20 minutes at 230 °C, well above the melting points of both PP and additives. Films were made by subsequently heat pressing the melt-blended mixtures. Heat-pressed films made from well-mixed melt blends were stored at room temperature until further analysis was performed. As shown in Figure 5, these films showed lower contact angles than those made through solution drop coating on Teflon.

The change in water contact angle was monitored over 7 days. Figure 5 shows the water contact angles after 1-day aging and 7-day aging. The IRGASURF, linear PEGs, and four-arm PEOs exhibited the lowest water contact angles, particularly after 7 days of aging, indicating that these additives showed the greatest promise for increased hydrophilicity. The dendritic polyesters, BOLTORN H30 and H40 additives, showed higher contact angles, especially after 7 days of aging, indicating that those additives tended to prefer the bulk rather than the surface.



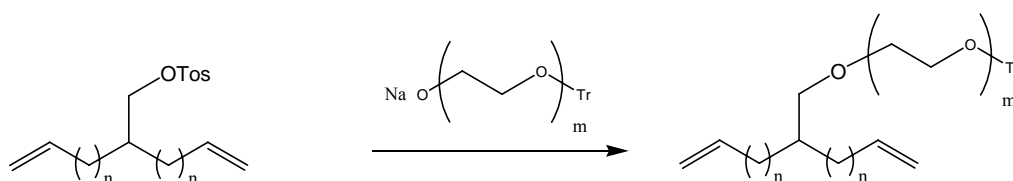
**Figure 5. Static water contact angles on films made from melt blended mixtures at 5 wt%.**

*Comb polymers synthesized at the University of Florida.* The synthesis of PE-g-PEO perfect comb polymers is being performed via the following scheme. First, the diene substrate, in this case a tosylate, is prepared through malonate modification (Figure 6) using alkenyl bromides of various ethylene run lengths ( $n = 3$  or  $9$ ).

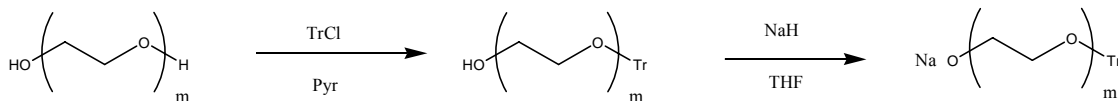


**Figure 6. Synthetic pathway to tosylate pre-monomer via malonate modification.**

The PEG branch is then added using nucleophilic substitution (Figure 7). Prior to substitution the oligoether chain ( $m = 4$  or  $8$ ) must be monoprotected with a trityl (triphenylmethyl) group to avoid side reactions and subsequently deprotonated to generate an attacking nucleophile (Figure 8).

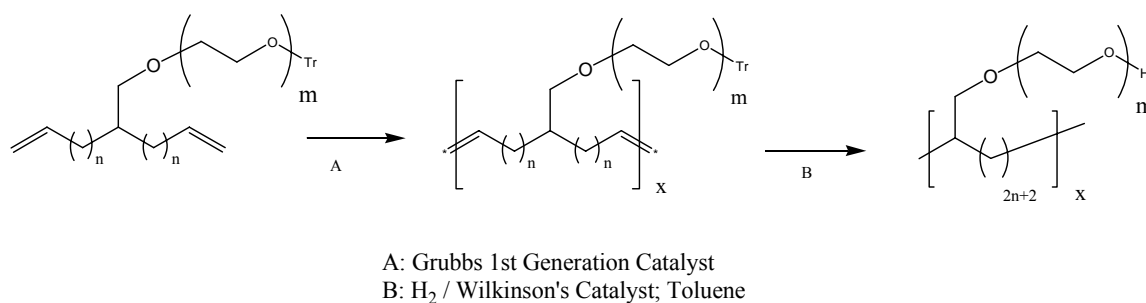


**Figure 7. Displacement of tosylate by oligoether graft.**



**Figure 8. Monoprotection and deprotonation of oligoether graft.**

The monomer is then polymerized in the bulk using Grubb's first generation catalyst. Following polymerization, the ADMET unsaturated polymer is treated with hydrogen and Wilkinson's catalyst to saturate the internal olefin and cleave to trityl protecting group, thereby affording the precision spaced PE-*g*-PEO comb polymer bearing a terminal hydroxyl group on the ends of the grafts (Figure 9).



**Figure 9. Polymerization of monomer and modification of ADMET pre-polymer.**

The synthesis of polymer 1 ( $n = 3$ ,  $m = 4$ ) has been completed. Polymers 2-4 ( $n = 9$ ,  $m = 4$ ), ( $n = 9$ ,  $m = 8$ ), ( $n = 3$ ,  $m = 8$ ) will be completed in the near future.

## SUMMARY:

Before making deep-grooved fibers, films made through drop coating and heat pressing from well-mixed blends were used to investigate the migration behavior of selected additives and their effectiveness in generating hydrophilic PP surfaces. Substrate plays an important role in inducing the additive migration direction. Hydrophilic additives are likely to migrate toward a substrate of high surface free energy; on the other hand, a low energy substrate drives hydrophilic additives back to the base polymer. Compared to drop coating, heat pressing melt blended mixtures showed better wettability for the PP films. Linear PEG and multi-arm PEO were observed to migrate to the surface and rendered the PP film more hydrophilic after 7 days of aging. Hydroxyl-terminated hyperbranched polyester migrated back into the base polymer over time.

**FUTURE GOALS:**

In pursuit of our goal to achieve more permanent and effective surface coverage of polyolefinic surfaces by hydrophilic migratory additives, PEG based systems with various chain lengths and terminal functional groups (-OH, -CH<sub>3</sub>, -NH<sub>2</sub>, *etc.*) will be employed and their migratory behavior will be investigated with respect to several factors such as aging, temperature, relative composition, and architecture. In the near future, controlled molecular weight of hyperbranched polyglycerol will be synthesized according to procedures in the literature [14]. Other classes of architecturally variant additives that are of particular interest are comb-like block co-polymers that offer a great potential in the form of structure and pendant group dependent surface and solution properties. Prof. Ken Wagener and his students at the University of Florida will synthesize more variants of the comb polymers as described above.

*Modeling:* For successful surface segregation, the additive and polymer should be largely incompatible, which precludes the use of Fickian-diffusion models. Therefore, based on prior work with simple linear additives, thermodynamics will be used to model the extent of surface segregation. For the most promising additives, kinetic studies will also be performed to determine “apparent” rate constants for predictive capabilities.

**Project website address:**

[http://www.ntcresearch.org/projectapp/project\\_leaders\\_area/project\\_info.cfm?project\\_id=M04-CL11](http://www.ntcresearch.org/projectapp/project_leaders_area/project_info.cfm?project_id=M04-CL11)

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