NANO-ENGINEERED ADDITIVES FOR ACTIVE COATINGS

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ABSTRACT

Novel additives for polymeric coatings have been developed based on modified hyperbranched polymers (HBP). The additives are polyfunctional, and have been prepared to spontaneously segregate to the surface of the polymer in which they are dispersed. They have been used to install "active" sites in polymeric films, with little or no change in the formulation, bulk properties, or application of the coating.

1. INTRODUCTION

Modern coating systems are challenged to meet a large number of performance characteristics. In the commercial realm, for instance, automotive paint must provide excellent corrosion and solvent resistance while maintaining high gloss and luster. Analogs for military coatings provide similar corrosion protection, while minimizing gloss and providing for camouflage schemes.

The next step for the evolution of coatings technology is the introduction of active sites to a painted surface. Many interesting technologies for surface modification exist in the realm of polymer chemistry, but few of them are amenable for use on a very large scale. Techniques such as chemical vapor deposition or atmospheric plasma treatment can effectively treat surfaces with exquisite control, but are often limited by substrate geometry and sample size. One notable, scaleable technique employs self-assembled monolayers, but the questions arise about the robustness and the stability of the system and therefore not suitable for real world use.
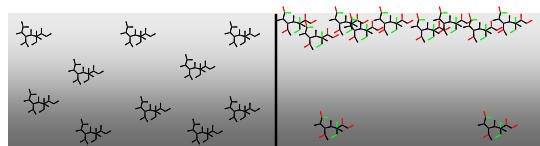
Bulk Distribution   **Surface Segregation**
Figure 1: Illustration of bulk and surface distributions

One potentially practical route to developing modified coating systems employs self-segregating additives, as illustrated in Figure 1. The image details the difference in distribution between an additive in the bulk and one concentrated at the surface. Surface segregation is attractive for coatings, as it reduces the total quantity required to achieve high concentration at the surface, and also minimizes impact of the additive on the bulk properties of the coating. The additives detailed herein have been applied to a range of model polymer and real-world coating systems, and demonstrate the formation of an "active" surface using standard application techniques.

2. EXPERIMENTAL DETAILS

Standard chemicals were obtained from Alfa-Aesar and were used as-received, unless otherwise noted. BASF Corp. provided the hyperbranched polyethyleneimine (PEI), while Perstorp, Inc. provided the hyperbranched polyester (PE). The perfluorinated components were either donated by DuPont or purchased from Exfluor Research Resolution Performance Products provided the aliphatic epoxy components. Noveon provided thermoplastic polyurethane (TPU).

Representative Synthetic Procedure: (note: alternative routes have been employed for the PE and PEI systems, and only one route is described for illustration) A PEI-HBP core (ca. 46 g, 418.2 mmol 1° amines) was suspended in dry THF (150 mL) in a 500 mL round bottom flask under dry nitrogen. Freshly prepared perfluorooctanoyl chloride (26.9 g, 62.3 mmol, prepared from perfluorooctanoic acid) was added via syringe over several minutes. Within 15 minutes the milky turbid suspension of PEI had formed a clear yellow solution, to which aliphatic epoxy was added (34.74 g, 120.3 mmol). The reaction was stirred 16 h at room temperature, and the solvents were then removed by rotary evaporation. The resultant viscous polymer was dissolved in methanol and transferred to a tared container, and was dried under heat (50 °C) and vacuum. This polymer began with an equivalent weight of 1° amines of ca. 110 g/mol; the final product contained residual 1° amines with an equivalent weight of ca. 454 g/mol. Preparation of the quaternary ammonium salt analog was accomplished using a two step procedure. The polymer was first treated with a bromo-alkyl acid chloride (room temp, dry THF) to install a halo-alkyl chain end via an amide linking group. The second reaction was performed in dry DMAc by combining the polymer with N,N-dimethyldecyl amine, at 80 °C for 48 h. The two steps proceeded in quantitative yield, and resulted in a glassy hygroscopic material with good solubility in methanol.

Film Preparation & Coating Analysis: To test the additive performance in polymer systems, a thermoplastic polyurethane (TPU) was chosen as a proxy for

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commercial coatings. Model formulations were obtained by combining a solution of the TPU with a solution of the additive. The formulations were then cast on a substrate, typically a glass microscope coverslip (18 x 18 mm) or a half-microscope slide, and then dried in a controlled environment. Dried films were evaluated using contact angle analysis. Near surface compositional depth profiling was performed using the Kratos Ultra X-ray photoelectron spectroscopy system, equipped with a hemispherical analyzer. A 100 W monochromatic $Al_{K\alpha}$ (1486.7 eV) beam irradiated a 1 mm x 0.5 mm sampling area. Survey scans were taken at pass energy = 80 eV. Elemental high resolution scans for C1s, O1s, N1s, and F1s were taken at pass energy = 20 eV. Kratos U software was utilized for all data analysis; linear background subtraction, curve fitting, peak integration, and charge compensation.

The activity of modified coating systems was evaluated using techniques according to ASTM E-2180, a method developed for the examination of hydrophobic coatings. In this method, a quantity of microorganism (ca. 10^6 organisms) is loaded onto a substrate (e.g. TPU-coated half microscope slide) with an agar slurry as the inoculum vehicle. The antimicrobial coatings are prepared at 1% by weight in a TPU polymer matrix of Noveon X-1150. The ASTM E-2180 test is run in triplicate for the 24 hour time points of controls and test samples, and duplicate for the 0 hour controls.

3. RESULTS & DISCUSSIONS

Several hyperbranched polymer systems were evaluated for their suitability for the modification technology developed by ARL (U.S. Army Research Lab). Two routes of modification have previously been identified by ARL, involving nucleophilic substitution of amines via Michael addition and epoxide-opening chemistry (Route I) or through melt condensation of an acid and alcohol (Route II). After the initial functionalization, the HBPs were further functionalized using acid chlorides followed by quaternization using N,N-dimethyl alkyl amines of varying lengths, with chain lengths of hexyl (C_6), decyl (C_{10}), and hexadecyl(C_{16}) under evaluation. One other route attached a biguanide to the periphery of the HBP. The secondary modification of the HBP cores is shown as Route III in Figure 2. Compositions for the prepared compounds can be found in Table 1, where extent of modification is expressed as a fraction of chain ends consumed by the indicated functional group. The bis-biguanido hexane used in this study is shown in Figure 3.

Figure 2: Synthetic Routes for HBP Modification
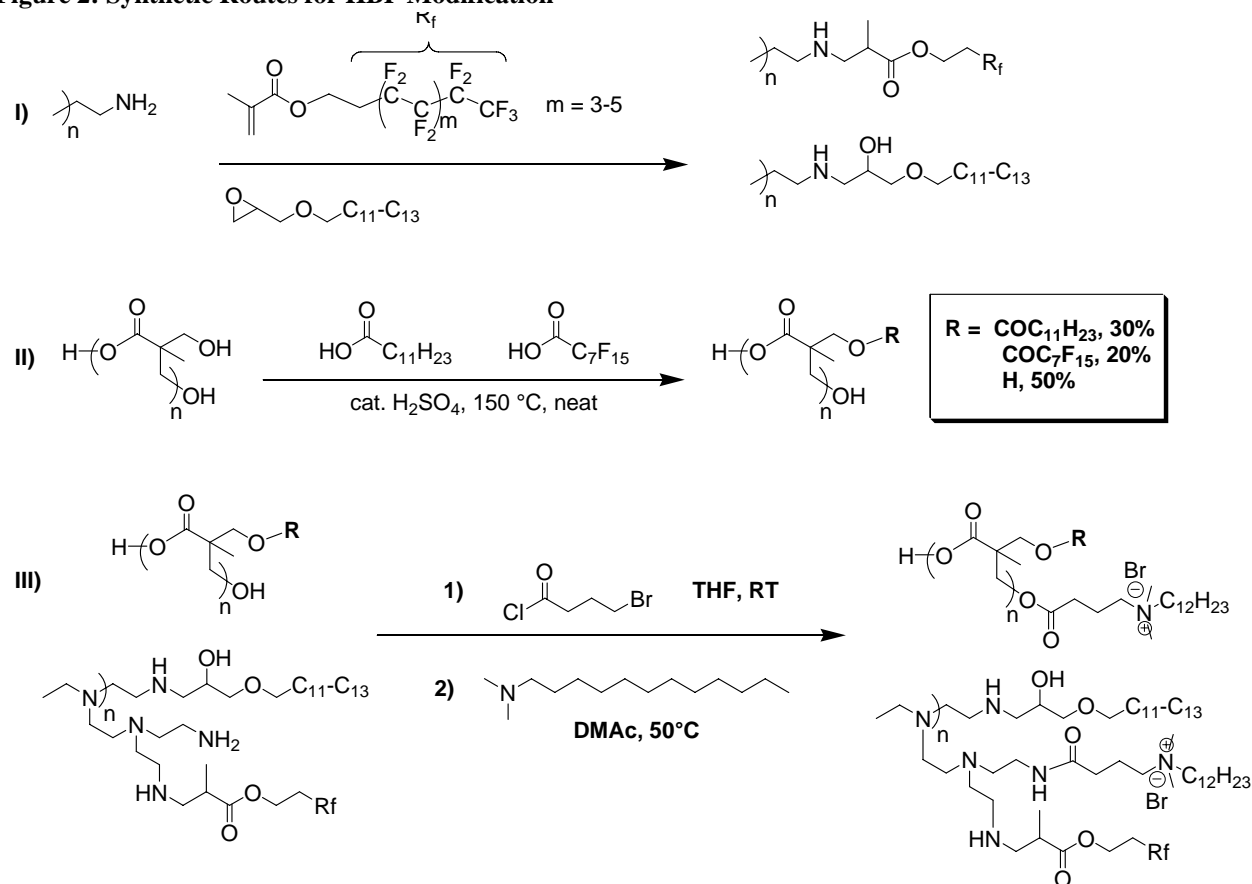
Sample	Base HBP	Mole Fract Perfluoro	Mole Fract Alkyl	Mole Fract Ammonium or Biguanide
ARL 1	PEI	0.2	0.4	0.0
ARL 2	PE	0.3	0.2	0.0
TSI 1	PEI (ARL 1)	0.2	0.4	0.4 (C_{10} quat)
TSI 2	PEI (ARL 1)	0.2	0.4	0.4 (Biguanide)
TSI 3	PE (ARL 2)	0.3	0.2	0.5 (C_{10} quat)

Table 1: End group composition of HBP-based additives

These materials were characterized by FT-IR (observed consumption of the methacrylate functionality by ca. 10 wavenumber shift in carbonyl absorption) and ^{1}H/^{13}C NMR. NMR confirmed the ring opening of the epoxide groups, and ^{13}C NMR clearly showed the installation of the amide chain ends. Unfortunately, NMR was not well suited for identification of the perfluoro chains, as the low mole fraction incorporated in the HBPs and the splitting of both ^{1}H and ^{13}C by the fluorine made interpretation of spectra difficult.
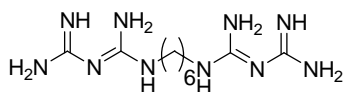
Figure 3: Bis-biguanide with C_6 linker

The base HBPs (**ARL 1** & **2**) demonstrated good overall solubility in common organic solvents. The quaternary ammonium salts maintained fair solubility in most solvents tested, and exhibited better water solubility than the corresponding core polymer. The biguanide containing material required more polar solvents to achieve full solvation, dissolving most easily in polar protic solvents (e.g. water, methanol).

The HBPs were tested for their ability to influence polymeric film surface properties using a model thermo-plastic polyurethane (TPU) system. The only "curing" mechanism involved in a TPU film formation is the gradual loss of solvent as it evaporates. The model systems, though, allow for careful study of film properties in the absence of competitive reactions and with fewer questions about kinetics. They were used to demonstrate the surface migration properties of the additives by preparing 1% additive formulations in dilute solution, using industrially applicable solvents (e.g. 2-butanone, or methyl-ethyl ketone, MEK). The films were cast onto glass substrates and dried under a solvent-saturated atmosphere, which lengthened drying times and generated thick films with marginal application defects.

The surface properties of the films were surveyed using contact angle analysis, that is a technique which characterizes the hydrophobicity or hydrophilicity of a surface based on its wetting characteristics. Several solvents are suitable for contact angle analysis, but the most widely employed is pure water. A graph of contact angle measurements is shown in Figure 4, where the influence of the additives is manifested as change in the observed hydrophilicity. This behavior is not observed in instances where the HBP does not migrate to the surface, as the properties of the TPU continue to dominate interactions. Data for the base materials **ARL 2** is not presented, as it can cause dewetting due to its strong influence on interfacial properties. In alternative TPU systems, though, it demonstrates a significant influence over observed surface characteristics.
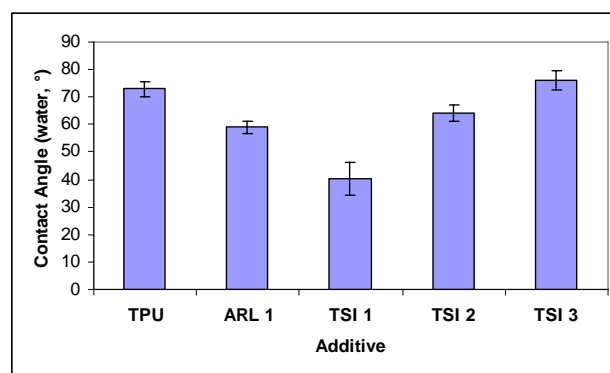

Figure 4: Contact Angle as Function of Additive, 1% loading

In addition to the contact angle results, XPS analysis has been used to profile the surface compositional profile of the films. Increases in surface levels of fluorine and nitrogen are typically observed if the PEI-based systems have migrated to the surface, while fluorine is the only indicator for the PE systems. Table 2 illustrates the compositional profiles observed. The levels of fluorine observed at the surface are quite high, considering the bulk quantities of fluorine in the films.

	C	F	N	O
TPU	70.97	0.00	5.50	23.53
ARL 1	68.24	6.95	9.93	14.89
TSI 1	72.98	2.80	7.14	15.85
TSI 2	74.98	0.10	5.51	19.33
TSI 3	74.40	3.09	4.05	18.17

Table 2: Surface Composition of Films

Hyper branched Polymer	Reduction C. albicans	Reduction E. coli	Reduction S. aureus
ARL 1		< 1 log	< 1 log
ARL 2		1 log	< 1 log
TSI 1	6 log	4 log	6 log
TSI 2	< 1 log	3 log	6 log
TSI 3		2 log	< 1 log

Table 3: Efficacy of 1 % Additive in TPU Matrix based on 6 log loading of organism

The model TPU systems were also examined with respect to their resistance to microbial challenges. Three organisms have been selected to represent gram positive (*S. aureus*), gram negative (*E. coli*), and fungi (*C. albicans*), providing a profile of broad spectrum activity. The results of this survey are provided in Table 3, and they demonstrate that the additives maintain substantial activity when incorporated into the TPU at 1% loading based on total solids.

While the results obtained in the TPU system are encouraging, there remained questions about the source of antimicrobial activity. One key attribute for preparing a persistent active surface is the prevention of leaching of the active component. Several commercial additives may be incorporated into a coating to grant it antimicrobial activity, but almost all rely on gradual release of the active component from the coating, leading to eventual depletion of the film. Small TPU samples were evaluated using a Kirby-Bauer test to probe for leaching of the active components. In the test, a sample of the film is placed on a mat of microbes (*E. coli* and *S. aureus*), and as the antimicrobial component diffuses from the substrate it generates a zone of clearing around the film via microbial death. For a TPU sample containing a small molecule quaternary ammonium salt, a zone of clearing of a couple millimeters was observed. There was no observed leaching of the HBP-based additives.

While the model systems described above have proven informative for the evaluation of the HBP-based additives, the TPU-based materials are not likely to yield commercially useful or viable systems. True sealants or coating systems employ reactive constituents, which cure or undergo spontaneous reactions to generate robust finish. One point of concern for the HBP-based additives has been the potential to react prematurely with the coating, preventing migration or resulting in tremendous shifts in performance of the coatings.

To test the influence of the additives on viable commercial coating systems, the HBPs have been incorporated into formulations based on polyurethanes (PU), polyureas (PUr), and epoxy systems. They were formulated to provide an ultimate composition of 1% additive based on the total solids content. The additives were dissolved in a solvent, generally methanol or MEK, prior to mixing to enable their dispersal in the coating formulation. Samples were prepared by spray or draw-down application, to give a dry final film thickness of 1 – 2 mils (ca. 25-50 μm). The films were cured at room temperature, and then evaluated using contact angle analysis and XPS. The film properties of the resultant coatings were also investigated.
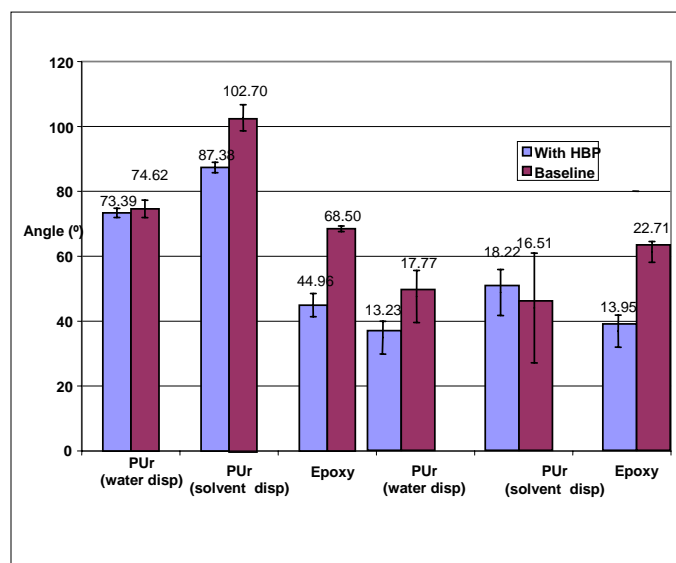

Figure 5: The advancing and receding contact angle for samples with (1 wt %) and without PEI-quat HBPs

Figure 5 illustrates the influence of the additive on the surface properties (wetting characteristics) of the resultant films. As was observed in the TPU systems, the coatings have exhibited a general decrease in contact angle with water, though the magnitude is much smaller for the crosslinked systems than for a low T_g thermoplastic matrix. While the increased hydrophilicity at the film surfaces suggests the migration of the HBPs, XPS can provide complementary compositional information.

	Composition - Atomic %			
Sample	C	O	N	F
Epoxy Baseline	82.05	14.36	3.29	0.30
Epoxy TSI 1	74.69	16.37	5.55	**3.39**
Epoxy TSI 3	77.15	16.12	3.62	**3.11**
PUr (water disp) Baseline	72.54	19.95	5.24	*ND*
PUr (water disp) TSI 3	70.32	16.20	7.04	**6.45**
PUr (solvent disp) Baseline	78.79	12.28	7.41	*ND*
PUr (solvent disp) TSI 3	71.53	14.79	5.15	**8.53**

Table 4: XPS results showing the elemental atomic percent of chemicals at the surface for the various military coatings with and without HBP.

Table 4 shows the measured elemental compositions of the formulations. The increase in fluorine levels at the film surfaces is interpreted as evidence of migration of the additives to the surface of the films, and correlates well with the observed contact angle results.

The motivating factor behind the use of self-segregating additives to modify coating systems has been to minimize the impact they have on the bulk properties of the matrix. Several physical characteristics of the cured coating systems have been investigated, including T_g and loss modulus.
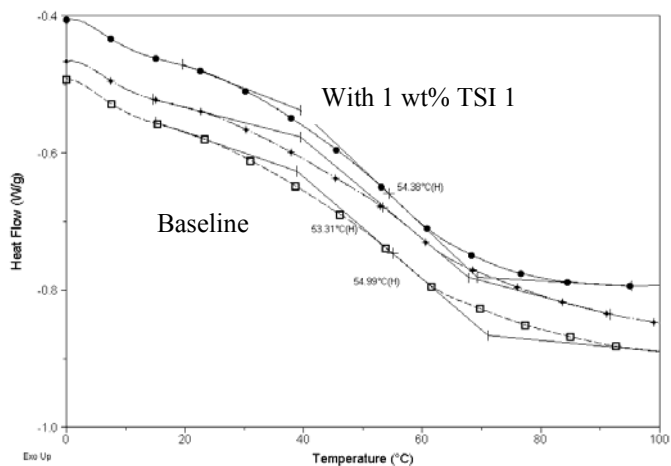

Figure 6: The DSC traces for PUr (water disp) with and without HBP.

The differential scanning calorimetry traces used to determine T_g values are presented in Figure 6 that demonstrated that there is little influence of the additive on the thermal properties of the coating. This was anticipated, as hyperbranched polymers typically exhibit very small T_g transitions, so observing its contribution to

the thermal profile would be very difficult. The other alternative would have been an overall lowering of the matrix T_g, if the additive acted as a plasticizer.
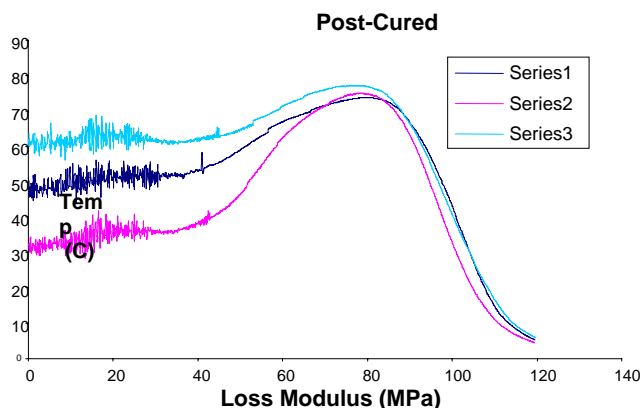

Figure 7: The loss modulus for PUr (solvent disp) for the baseline (blue), 1 wt% TSI 1 (pink), and 1 wt % TSI 3 (light blue).

The influence of the additives on the overall film appears slight, as measured using glass transition temperature and loss modulus. The films were also evaluated for their efficacy as biocidal surfaces using the ASTM E-2180 technique. In these experiments, summarized in Table 5, the additives are less effective in cross-linked systems for the overall biocidal activity. This eventuality was not completely unforeseen, as the cross-linked nature of the PU/PUr/Epoxy films leads to decreased mobility for the additives at the film surface.

Hyper branched Polymer	Reduction C. albicans	Reduction E. coli	Reduction S. aureus
TSI 3	2 log	1 log	6 log

Table 5: Summary of 24 Hour ASTM 2180 Tests with 1 wt % Additive in PUr (solvent dispersible) based on 6 log loading of organism

4. CONCLUSIONS

There is a tremendous need to improve coating systems by incorporating reactive moieties that can active decontaminate various environmental pathogens. The objective of this effort was to develop affordable nanotechnology-based solutions that can be directly integrated into polyurethanes used by the Army while maintaining all military-specified properties. This was accomplished through tailored modification of the surface of the coating by self-assembling nanoparticulate additives resulting in local changes in surface properties.

The Army presently spends over $100M on CARC top-coats annually. Improved performance and reduced coating costs will have widespread and significant impact on Army materiel.

The technology presented here represents a significant advancement over known systems in that it 1) combines the polyfunctional nature of non-entangling additives, such as hyperbranched polymers, to provide a tailored material that 2) is soluble or dispersible within a paint system 3) migrates to the air interface 4) transports active antimicrobial or decontaminating agents to that interface, 5) chemically reacts with the polymeric binder of the coating to prevent leaching of the active agent and 6) is useable in various types of coatings, including epoxy primers, polyurethane topcoats, and latex systems. A strong potential exists for using traditional coatings materials with a small quantity of additive providing substantial antimicrobial and decontaminating activity. Furthermore, these results indicate that self-segregating additives have the ability to transport a myriad of active materials to the air/polymer surface of a coating; thus, acting as a "*Universal Transport Vehicle*." These materials may also have potential use in coated fabrics, latex paints, etc. for military as well as civilian applications.

5. ACKNOWLEGEMENTS