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A Hybrid Experimental and Model-Based Methodology for the Formulation of Self-Stratifying Coatings

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Short Abstract

A systematic procedure to formulate self-stratifying coatings using a hybrid experimental and model-based methodology has been developed. Herein, first different combination pairs of polymeric resins are screened through computer-based algorithms. These make use of models to predict the physicochemical properties which are responsible for the different factors that affect self-stratification. A few promising candidates for preparing the formulations are selected. First, only the polymeric resins are studied for phase separation. The resins showing phase separation are combined in optimum quantities to produce 500 μm films (wet film thickness) on plastic substrates, which are then evaluated for the degree of stratification using FTIR-ATR and SEM-EDS analysis techniques. The difference in the absorption spectra of the top and bottom surfaces of these films as well as a significant difference in topography of the microscopic images across the cross-section confirmed the occurrence of stratification. Following this evaluation, the effect of solvents and pigments on the extent of stratification will also be considered.

Introduction

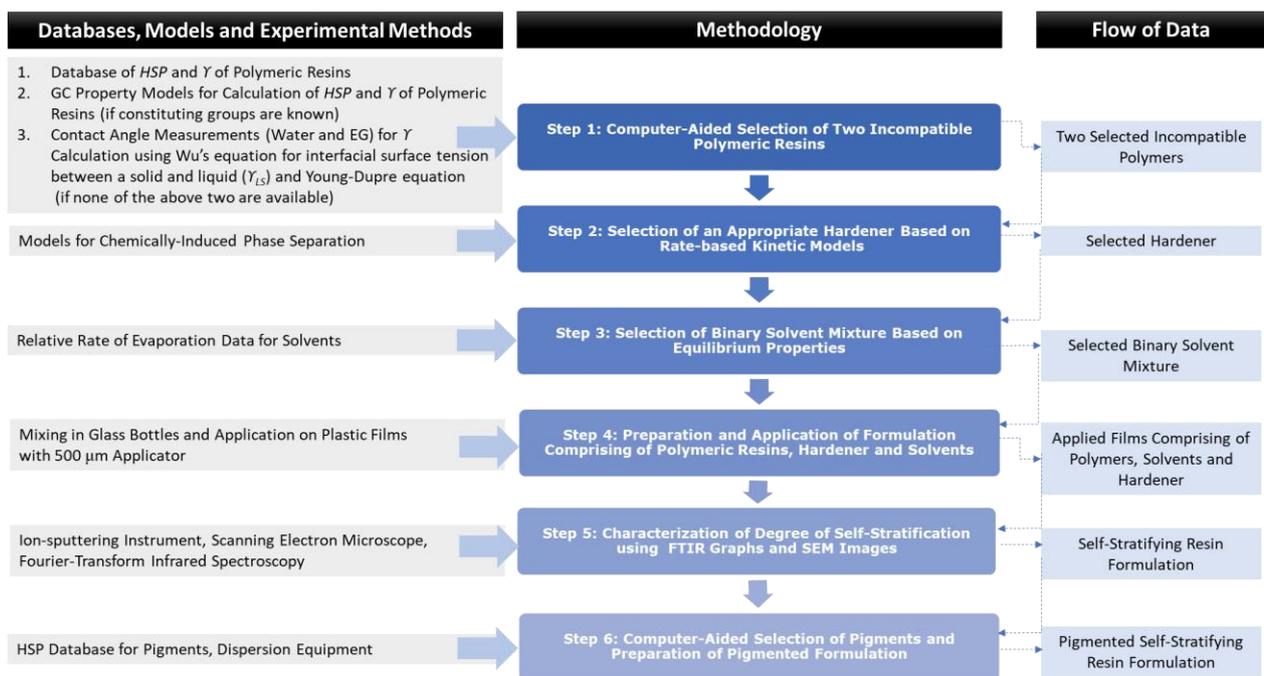
Multilayer coatings are commonly applied in the automotive, aerospace, general industrial, architectural and transportation industries. In most cases, an intermediate coat or a primer coat is applied, dried or cured to provide foundation for good adhesion or to function as a barrier/corrosion control layer. However, these multi-layered systems require complex application, curing/drying procedures, and extensive time for processing. Therefore, several attempts to formulate a self-stratifying coating system have been made [1–4] with the foresight to eliminate the problems encountered with interlayer adhesion, long curing times for individual layers and overcoating of the substrate (minimum interval: 1.7 times the dry film thickness, maximum interval: 3 times the dry film thickness).

In this work, the aim is to systematize and accelerate the process of formulating a self-stratifying coating by using physicochemical property models and generic thumb rules for a fast screening of potential ingredients and then testing only a few promising candidates for formulation in the laboratory. An algorithm has been developed, which can enable a formulator to select two polymeric resins that can self-stratify is affected by the following five quantities: ‘volume of overlap of the solubility spheres of the resins’, ‘difference in surface free energies of resins and substrate’, ‘crosslinking kinetic rate of hardener and resins’ and ‘carrier (solvent / water) rate of evaporation’. The relevant properties with respect to each of these quantities are consolidated and consequently used to calculate them. In the case where all conditions on these properties with respect to each of these quantities is satisfied, the polymeric resins would be regarded as “self-stratifying”. The formulations consisting of the selected polymeric resins are then tested for stratification using FTIR-ATR and SEM-EDS analysis techniques. This ensures that fewer resources are spent on experiments and a substantial amount of time is saved.

Methodology

The developed methodology outlined in Figure 1 comprises of six steps. First, incompatible polymeric resins are chosen on the basis of the overlap of their solubility spheres, which is calculated using the resin Hansen Solubility Parameters (*HSP*) and a difference in the surface tension (γ) of these polymeric resins. If the *HSP* and γ data of the considered polymeric resins is not available, group contribution (GC) models for determining these properties could be used. In absence of their data or model, experiments to determine these properties of the resins could be conducted.

Next, the hardener that could crosslink with one of the resins is selected using the kinetic data of the reaction between this hardener and the resin. In case the rate of reaction of the hardener with one of the resins is faster compared to the other thermosetting resin, or the hardener is unreactive with a thermoplastic resin in the chosen system, a chemically induced phase separation of the binary polymer system is likely to occur.



*HSP: Hansen Solubility Parameter; γ : Surface Tension; GC: Group Contribution

Figure 1: Workflow for the Methodology to Formulate a Self-Stratifying Coating

Next, the binary solvent mixture for the system is selected such that one of the two polymeric resins is soluble in the solvent with a low value for the relative rate of evaporation while both the resins are soluble in solvent with the highest evaporation rate. Now, that the resins, hardener, and the solvent mixture to prepare a self-stratifying formulation are selected, the formulation is prepared in glass bottles and applied on plastic laminates using a 500 μm applicator. To test for stratification an FTIR-ATR analysis of the top and bottom surfaces of the films is made. Besides, a SEM-EDS image analysis is used to confirm the stratification based on difference in the topography. If a self-stratifying polymeric system is obtained, then the possibility of dispersion of pigments is studied using the HSP data and the pigments that satisfy the dispersibility conditions are tested using the dispersion equipment.

The coating free film was cut in liquid nitrogen before making the analysis of its cross-section. Then the silver-metallization of the sample was performed using the ion-sputtering instrument in order to make the coating film conductive so that the SEM analysis can be performed. Further, for performing the SEM analysis, a high vacuum mode, a Working Distance (WD) of 10 mm, an Accelerating Voltage (HV) of 5 kV, a Scanning Rate Period of 5 μs and Everhart-Thornley Detector (ETD) is used.

Results & Discussion

Six formulation recipes comprising of an acrylic polymer and two-component epoxy polymer as well as a hardener were tested for the possibility of stratification using FTIR analysis. All the six formulation recipes were applied on plastic substrates. The details of these recipes are summarized in Table 1. The polymeric resins in these recipes were chosen after screening through the properties of 86 pairs of resins and using the theoretical models to calculate the relevant quantities that determine the possibility for self-stratification.

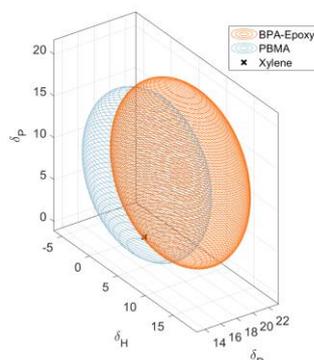


Figure 1. Solubility Sphere Overlap of PBMA and BPA-Epoxy Polymeric Resins

The resins chosen for the first four formulations have a difference in surface tension of greater than 7 Nm^{-1} while the volume of overlap of the solubility spheres is less than 60%. A diagrammatic representation of the same has been shown in Figure 1. The 3D Hansen solubility parameters of the solvent chosen for the system lies in the overlapping region of their solubility spheres.

Table 1. Formulation Recipes Tested for Self-Stratification

	Raw Material	Sp. Gr.	Volume Solids	Weight Solids	EW	Weight (g)
1.	PBMA solution in Xylene	0.95	0.363	0.4	--	10.00
	Liquid BPA epoxy (middle MW soln in Xylene)	1.17	1	1	187	7.42
	3-(Diethylamino)propylamine	0.826	1	1	65	2.58
						20.00
2.	PBMA solution in Xylene	0.95	0.363	0.4	--	10.00
	Solid BPA epoxy (middle MW soln in Xylene)	1.1	0.722	1	666.67	9.11
	3-(Diethylamino)propylamine	0.826	1	1	65	0.89
						20.00
3.	PBMA solution in Xylene	0.95	0.363	0.4	--	10.00
	Liquid BPA epoxy (middle MW soln in Xylene)	1.17	1	1	187	8.46
	m-xylene diamine	1.052	1	1	34	1.54
						20.00
4.	PBMA solution in Xylene	0.95	0.363	0.4	--	10.00
	Solid BPA epoxy (middle MW soln in Xylene)	1.1	0.722	1	666.67	9.51
	m-xylene diamine	1.052	1	1	34	0.49
						20.00
5.	Aq. Dispersion of Solid Epoxy Resin	0.95	--	0.4	525	7.00
	Non-ionic Aq. Dispersion of Modified Polyamine Adduct	1.17	--	1	250	3.00
	Silicone Resin Emulsion	1.052	--	0.45		10.00
						20.00
6.	Aq. Dispersion of Solid Epoxy Resin	0.95	--	0.4	525	7.00
	Non-ionic Aq. Dispersion of Modified Polyamine Adduct	1.17	--	1	250	3.00
	Silicone Resin Emulsion	1.052	--	0.6		10.00
						20.00

Key: Sp.Gr.: Specific Gravity, EW: Equivalent Weight, PBMA: Polybutylmethacrylate, BPA: Bisphenol-A Epoxy, Aq.: Aqueous

From the FTIR analysis it was seen that among the four solvent-based formulations, the solid BPA epoxy (middle MW Bisphenol A solution in xylene) wherein DEAPA, 3-(Diethylamino)propylamine has been used as the hardener and combined with the thermoplastic resin, PBMA, has shown self-stratification. The absorption spectra recorded for the top and bottom surfaces for this formulation are shown in Figure 2. However, among the two water-based formulations none of them show a difference in the absorption spectra on the top and bottom surfaces. Both the spectra correspond to that of polymethylsiloxane (Figure 3).

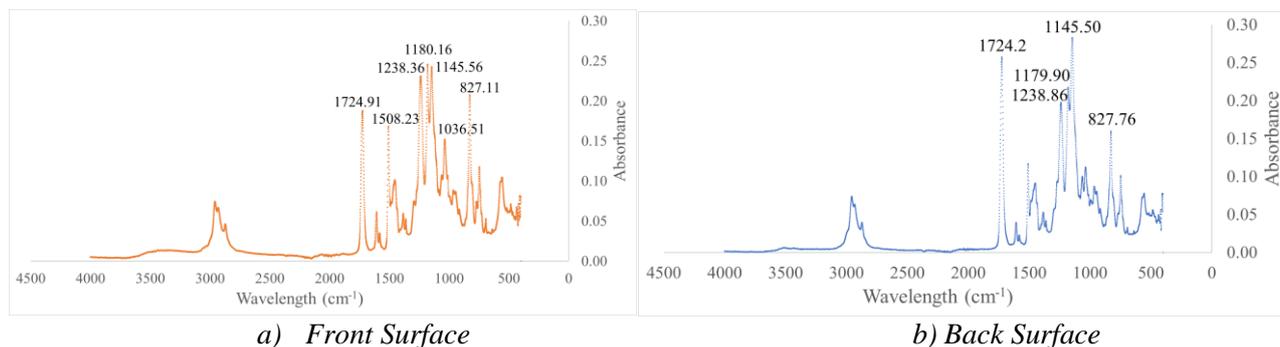


Figure 2: FTIR Absorption Spectra of the Films Corresponding to PBMA and Epoxy Resin Respectively

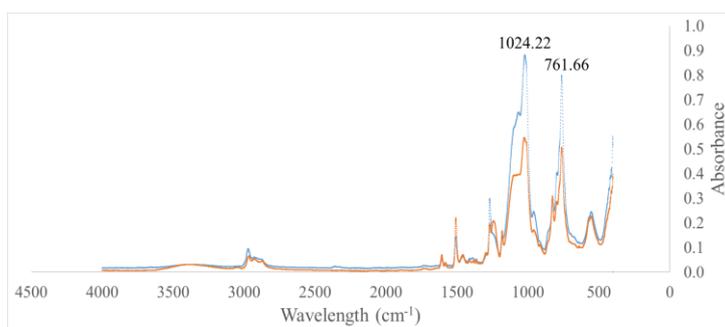


Figure 3: FTIR Absorption Spectra of Front and Back Surfaces of the Films Corresponding to Polymethylsiloxane

In order to confirm the FTIR results, SEM analysis of these two formulations has also been performed.

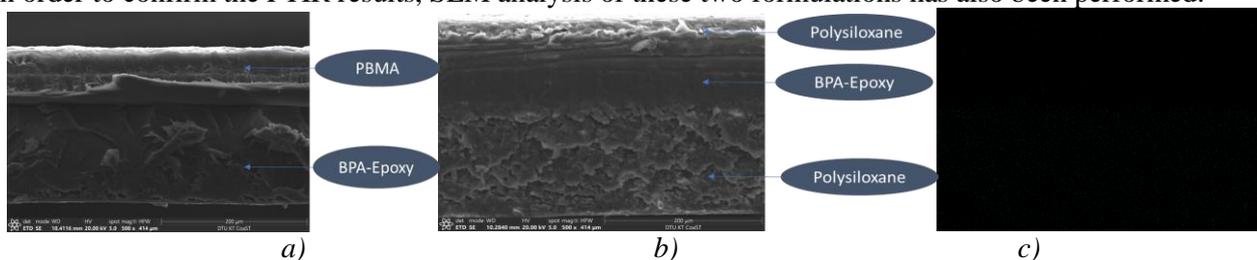


Figure 4a): SEM Image for 40% wt. PBMA in Xylene + Bisphenol A-based Epoxy in Xylene + 3-(Diethylamino)propylamine

Figure 4b): SEM Image for Aq. Dispersion of Solid Epoxy Resin + Non-Ionic Aq. Dispersion of Modified Polyamine Adduct + 45% Solids Silicone Resin Emulsion

Figure 4c): EDS Mapping of Si particles for Aq. Dispersion of Solid Epoxy Resin + Non-Ionic Aq. Dispersion of Modified Polyamine Adduct + 45% Solids Silicone Resin Emulsion

From the SEM imaging analysis for the PBMA-BPA epoxy resin combination when DEAPA is used as the hardener, a clear distinction of the top and bottom layers is seen (Figure 4a). However, for the case of the silicone-epoxy resin emulsion, three distinctive layers are seen (Figure 4b). The topmost and lowermost layers are rich in silicone, whereas the middle layer is rich in the epoxy resin (Figure 4c).

Conclusion and Future Work

When plastic is chosen as the substrate, stratification of a binary blend comprising of a thermoplastic and thermoset resin involving a crosslinking agent is distinctly seen for an acrylic-epoxy resin system with an amine hardener. Moreover, for the aqueous emulsion containing silicone three distinct layers are observed.

Theoretically, it is known that the stratification can be further enhanced if two solvents having a significant difference in the relative rate of evaporation are used. Therefore, for the future work, it is proposed that the acrylic solution is formulated in methyl ethyl ketone (MEK) (relative rate of evaporation = 3.8) while the epoxy is formulated in xylene (relative rate of evaporation = 0.6). Moreover, MEK is an environmentally friendly solvent with non-toxic vapor content and can hence be used to formulate a greener coating.

Acknowledgements

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