

## EPOXY : ANHYDRIDE – 2 PHASE SYSTEMS FOR TOUGHENED APPLICATIONS

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The quest for polymers that can outperform metals in every way has gone on since the invention of the earliest plastics over a hundred years ago. Although composites consisting of resin, filler and/or fiber have replaced metals used for golf shafts and tennis rackets they are just beginning to make inroads into structural members for airplanes. The much-anticipated Boeing 787 Dreamliner and the Airbus A350 will be the first commercial planes to have a majority of their structural components fabricated from non-metallic composite materials. Why has it taken so long? I cannot remember a time when fishing poles were not made from fiber-reinforced plastics. In fact almost every sporting good from skis to golf shafts has transitioned from either wood or metal to composites. The answers to this question may vary depending on who you ask but for many people in aerospace the major concern has been damage tolerance. After all, any metallurgist will tell you that if you hit even a strong, high Tg composite hard it will crack whereas metal will only dent. In general, if you make a composite flexible enough to withstand the force of the impact it will undoubtedly sacrifice much of its strength.

This paper will explore a new approach for the solution of the paradox. How can you make a strong, high Tg plastic that is, at the same time, flexible enough to absorb destructive forces with minimal lasting deleterious effect.

Since epoxies are the most common resin for the production of high performance composites we have concentrated our work on epoxies, in particular, anhydride cured epoxies.

Toughening epoxy resins is nothing new. Epoxies can be formulated to impart properties ranging from high Tg, strong and hard materials to flexible, soft, low Tg systems. Unfortunately, the later tend to have good impact resistance and superior toughness while the former tend to be brittle. Many end uses for epoxies whether in adhesives, coatings, encapsulants or structural composites require a combination of these properties and excellent results can be achieved via the proper choice of resin, curing agent and flexibilizer. However, there are certain applications that require a high Tg and high flexural and tensile strength while still requiring resistance to cracking or delamination when exposed to impact, sudden temperature change, or, differences in thermal expansion when metal or ceramic inserts are incorporated.

There have been many attempts to solve this problem and significant progress has been made. The early work centered on the incorporation of plasticizers both reactive and non reactive as well as the incorporation of liquid rubbers. More recent work includes core shell additives and hybrid systems where two dissimilar polymerizations occur independently such as a flexible acrylic within an epoxy matrix. Other work centers

around finding ever stronger resins and curing agents that can be combined with more flexible ones to achieve the desired results.

In our work we theorized that it may be possible to have two different curing agents that are completely compatible as monomers but can be made incompatible as they polymerize. It was our hope that we could transition a homogeneous solution of soluble monomers into a heterogeneous polymer. If the polymerization occurs in a single stage but naturally separate due to changes in solubility it would be possible to form a heterogeneous polymer. And if the different portions of this polymer had different physical characteristics such as hard versus rubber like a phase separated polymer would result. To put it another way, our hope was that if we can get the materials to separate as they polymerize we would be able to have a resulting polymer that will exhibit the strong high Tg properties of the high Tg curing agent without compromise while imparting the flexibility of the lower Tg curing agent in a way that maximizes its contribution. Similar to the core shell technology we wished to create pockets of cushioning within a strong high Tg matrix, but unlike core shell technology we wished to maintain the cross-link density and tensile strength.

What we wished to achieve was a true two-phase system where in both the solid high Tg phase existed uncompromised while pockets of a rubbery phase epoxy formed within to alleviate stress and provide impact resistance. To achieve this incompatibility we had to find an additive that would be soluble and compatible in an uncured monomer solution consisting of one or more epoxy resins and one or more anhydride curing agents, but would become incompatible as the epoxy anhydride cured. We also had to find a flexible anhydride where this same additive would be compatible both in the uncured state as well as the cured state. It was hoped that this difference in the solubility of the additive as cure proceeded would be enough to force a phase separation and rather than having a random flexible anhydride within the matrix clusters of these flexible anhydrides would be created forming a two phase block copolymer.

For the purpose of this paper we will refer to this additive as the phase separation catalyst {PSC}. At the bequest of our patent attorney I am not at liberty to disclose its nature.

The first part of our work consisted of finding a PSC that would be soluble in a pure anhydride and a standard bis A epoxy. For this stage of our work we used MHHPA, methyl hexahydrophthalic anhydride with the methyl group solely in the delta 4 position. We also used a standard bis A epoxy. Over the years we had stumbled upon several classes of additives that caused cloudiness in cured epoxy anhydride systems. We had advised customers to avoid these additives in the past but for this work they provided a starting point for our investigation. It was interesting to note that even small amounts, less than one tenth of a percent of these additives had the ability to transform a clear light yellow solution into a completely opaque beige casting upon cure. While without the additive a perfectly clear slight yellow casting would result. Figure 1 illustrates this effect.

The second part of our search for a phase separation catalyst {PSC} was to see if the incompatibility results that we achieved with the MHHPA cured epoxy system could be avoided with a different anhydride source. The anhydride chosen for this was AC-39 which is linear with long carbon chains to provide flexibility where as the MHHPA has a cyclic structure with a pendant methyl group to inhibit rotation and increase the Tg. With AC-39 and epoxy resin the chosen PSC was soluble in both the monomeric solution as well as in the cured polymeric casting and the cured sample remained clear even with the PSC included.

Once a PSC was selected that met the requirements of 1) Being completely soluble in the un-cured epoxy and high Tg anhydride blend but 2) incompatible in the cured epoxy – high Tg anhydride while 3) being completely soluble and compatible with both the uncured and cured epoxy and low Tg anhydride; it was decided to test our phase separation theory by looking at the properties of bis A epoxy cured with mixtures of AC-39 and MHHPA with and without the PSC. Tgs were measured on TA Q200 DSC. For most of this work a less pure MHHPA that also included some MTHPA was used this product is referred to as MTHPA-C and yielded even more levels of separation with better physical properties.

What we found is that the MTHPA-C and standard bis A epoxy (formulation 1) had a clear Tg at 136 C. We then added approximately 0.5% of our PSC (formulation 2) and ran a DSC scan on the cured sample. What we saw was a very different curve. The PSC addition lowered the Tg which was not surprising however, rather than a single Tg there were now two, one at 134 C and another at 108 C. Formulation 5 was the original pure delta 4 MHHPA since there is only a single anhydride even with the PSC present only a single Tg resulted at 141 C. Formulas 3 and 4 included AC-32 an aromatic dianhydride with and without the PSC. Here as with the MTHPA C the PSC lowered the Tgs but since the PSC was equally incompatible in the AC-32 as it was in the MTHPA-C no additional phase separation was detected. Formulations 6 and 9 included PAPA a linear poly anhydride. Here once again sample 9 which included the PSC showed an additional Tg and also exhibited a lowering of the glass transition temperatures. Formulations 7 and 10 were the samples our PSC was chosen for. Here we see a minimal lowering of the upper Tg when the PSC is present but three Tgs are evident as compared to one without the PSC. Samples 8 and 11 showed the effect of the PSC on a blend of MTHPA-C and Meth-E which is a bicyclic anhydride with a pendent methyl group. Here the PSC caused only a slight lowering of the Tg but no addition transitions were present, the solubility profile of the PSC being the same in both the cured Meth-E epoxy as in the cured MTHPA-C epoxy. With samples 12 and 14 we tried to look at the effect of the level of PSC. We used a MTHPA-C/ AC 39 blend and a level of 0.5% and 0.1%. Here we achieved the same distinct Tgs however the reduced level of PSC raised the highest Tg significantly. Formulations 13 and 15 compared two factors. They both had reduced levels of AC-39 and 15 had a reduced level of PSC. Here the higher levels of PSC gave more separation however the reduced level of PSC increased the upper Tg significantly. Formulation 16 was a control for the work on the MTHPA-C and AC-39 system. Here as predicted we have less separation than with formulation 12 but do not have a higher upper Tg. Formulations 17 and 18 compare epoxy cured with only AC-39 at the two

different levels of PSC. Here, as predicted, since there is only one anhydride and no visible incompatibility a single Tg exists. Also even in a system such as this where the PSC is soluble higher levels of PSC do lower the Tg considerably. We then looked at the effect of lower PSC levels on our high Tg MTHPA-C system alone (formulation 19). When compared to formulation 2 once again we see lower PSC levels yielding higher upper Tg results. Finally we looked at AC-39 in combination with Meth-E. Here we got a surprising result. Formulation 20 that contains the PSC had a significantly higher upper Tg than formulation 21, which did not have PSC. The results are tabulated in tables 1 and 2.

. We then prepared samples for physical testing which included three point bend testing, hardness testing and break characteristics. Here the PSC was found to have significant advantages. For example the flexural modulus for formulation 1 was found to be 308,000 psi while with the PSC (formulation 2) it increased to 392,000 psi. When comparing formulation 13 and 14 the flexural strength remained almost the same when the amount of AC-39 was increased 5 fold combined with the introduction of PSC. When comparing levels of PSC as is the case in formulation 12 and 14 as well as 13 and 15 lower levels of PSC not only raise the high end Tg but also increase the flexural modulus.

Finally we sent out a sample to have the flexural strength run as a function of temperature with and without the PSC. Here the results were dramatic and the true value of this discovery can be discerned. The sample with the PSC maintained a 20% higher modulus than the sample without PSA up to the Tg. In addition the failure mode showed the characteristic whitening at the stress point that is associated with two phase systems.

Conclusion: A PSC (Phase separation catalyst) has been found that is soluble in uncured epoxies and anhydrides but is insoluble in epoxies cured with cyclic anhydrides. When linear anhydrides are introduced internal phase separation occurs during the polymerization process resulting in toughened polymers that retain much of their untoughened properties with respect to hardness, flexural modulus and flexural strength. In addition the failure mode is altered and the impact resistance improved. This technology is ideally suited for structural composites as well as potting compounds and adhesives that have to maintain their physical properties at high temperature yet be malleable enough to absorb stress caused by thermal expansion and shrinkage, vibration and impact.

### Formulation Key

#	EPOXY	MTHPA-C	AC-39	MethE	PAPA	AC32	BV7	PSC
1	100	80	--	--	--	--	1	--
2	100	80	--	--	--	--	1	1
3	100	60	--	--	--	30	1	--
4	100	60	--	--	--	30	1	1
5	100	80 (MHHPA)	--	--	--	--	1	1
6	100	60	--	--	30	--	1	1
7	100	60	30	--	--	--	1	1
8	100	60	--	30	--	--	1	1
9	100	60	--	--	30	--	1	--
10	100	60	30	--	--	--	1	--
11	100	60	--	30	--	--	1	--
12	100	55	55	--	--	--	1	1
13	100	75	10	--	--	--	1	1
14	100	55	55	--	--	--	1	0.2
15	100	75	10	--	--	--	1	0.2
16	100	55	55	--	--	--	1	--
17	100	--	200	--	--	--	1	1
18	100	--	200	--	--	--	1	0.2
19	100	80	--	--	--	--	1	0.2
20	100	--	10	75	--	--	1	1
21	100	--	10	75	--	--	1	0

## Formulation Characteristics

#	Appearance	Durometer Number	Break Characteristics	Flexural Modulus (x10 <sup>5</sup> psi)
1	Clear	84.5	Moderate force, explosive 5°-10°	3.08
2	Yellow/Beige Cloudy	83	Moderate force, small flex, exploded 5°-10°	3.92
3	Clear			
4	Yellow/Orange Cloudy			
5	White Cloudy			
6	Cloudy, orange/white bi-layer			
7	Yellow/Beige Cloudy	79	Shattered, no lines, ~15°	
8	Cloudy Orange			
9	Clear			
10	Clear	76.7	Smooth snap, no lines ~15°	
11	Clear			
12	Orange mostly cloudy	82	Lot of force, shattered, stress line ~10°	2.63
13	Yellow/Beige Cloudy	82.3	No force, weak <5°	2.97
14	Slightly cloudy	72.3	Easy break, smooth 5°	2.82
15	Orange mostly cloudy	79.5	No force, smooth <5°	3.29
16	Clear	76	More force, small flex, textured break 5-10°	
17	Clear	59	Little force, no break	
18	Clear	61	Little force, no break	
19	Yellow/Beige semi-Cloudy	83.8	Moderate force, small piece came off each time, textured break 5-10°	
20	Orange/Beige Cloudy	81.8	Moderate force, no lines, not as explosive, small pieces, 5-10°	
21	Clear Orange/Brown	80.8	Little force, no lines, not as explosive, small pieces, 5-10°	

T<sub>g</sub> Analysis

#	Number of Transitions	Description	Transition Temperatures			
			1	2	3	4
1	1	Large	136.0°C			
2	2	1 tiny, 2 medium	107.5°C	133.7°C		
3	5 (1)	1 medium shallow, others tiny negligible	118.1°C	134.7°C	186.2°C	211.5°C
4	5	1,2,4,5 small, 3 medium	102.1°C	122.3°C	142.8°C	185.9°C
5	1	Medium	140.6°C			
6	2	First shallow small, second large	50.8°C	89.7°C		
7	3	Small	69.3°C	90.9°C	98.5°C	
8	1	Medium	140.6°C			
9	1	Medium	98.9°C			
10	1	Medium, shallow	103.8°C			
11	1	Medium	138.5°C			
12	3	1 medium shallow, 2 small, 3 small shallow	53.6°C	85.6°C	92.2°C	
13	2	1 small, 2 medium	51.7°C	114.3°C		
14	3	1,2 small, 3 tiny	51.4°C	84.7°C	126.8°C	
15	2	1 medium, 2 large	52.1°C	116.7°C		
16	2	1 small shallow, 2 medium shallow	51.7°C	87.5°C		
17	1	Small, extremely shallow	41.1°C			
18	1	Small shallow	54.9°C			
19	2	1 small shallow, 2 medium	51.8°C	138.8°C		
20	2	1 small shallow, 2 medium shallow	51.0°C	127.6°C		
21	2	1 tiny very shallow, 2 medium diffuse	51.5°C	109.6°C		

Flexural	Strength	Instron
	#15 w/o PSC	#15
MOD	413	437
STRAIN	9.3	10.2
YIELD	9.1	12.2
A/C	1.65	1.75
STRESS	18.9	20.9
T <sub>g</sub>	110C	110C
		2 phase stress whiten

