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A New Amine Promoter for Low-temperature Cure of MEKP Initiated Unsaturated Polyester Resin Systems

by

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Abstract

A new amine promoter was developed and its curing properties in unsaturated polyester systems were studied in comparison with DMPT and DMA. The results showed that this amine has better curing properties than DMPT and DMA at sub-ambient temperature. The resultant cured resins derived from this amine had better mechanical properties, better water/solvent resistance and lower color than those resins cured with DMPT and DMA.

Introduction

Unsaturated polyester resin is one of the most commonly used thermosetting polymers in both industrial and civilian world. As a low-cost, rigid, high strength-to-weight material, one can find its products in the form of mechanical parts, pipes, tanks, electronic gears, etc. The reinforced unsaturated polyester resin is one of the major raw materials for making house-wares, furniture, automobiles, tools, boats, bathtubs, and many more products [1, 2].

Usually unsaturated polyester resins are viscous liquids consisting of oligomeric unsaturated polyester and polymerizable diluents (e.g. styrene or acrylate/methacrylates), as well as polymerization inhibitors. They can be cured to give insoluble, infusible solid plastics through a free radical curing process. Organic peroxides are employed as free radical initiators while tertiary aromatic amines and some organic metal salts, such as cobalt naphthenate, are used as curing promoters if needed [1]. It is well known that tertiary aromatic amine and cobalt naphthenate can significantly reduce the decomposition temperature of peroxides via chemical reduction processes.

Although all tertiary aromatic amines are able to promote the production of free radical, the efficiency of each amine is quite different and depends on the structure of the amine molecule [3-5].

Recently, Albemarle Corporation developed a new tertiary amine, referred to as Experimental Promoter A, or XP-A, which have some unique curing properties under certain curing conditions. In this paper, we will compare it with N, N-dimethyl-*p*-toluidine (DMPT) and N, N-dimethylaniline (DMA) on aspects such as the curing properties and physical properties of the cured unsaturated polyester resins.

Experimental

Materials

The resin used throughout the study was an unpromoted unsaturated polyester resin Aropol 7221 (Ashland Specialty Chemicals). Styrene was obtained from Aldrich Chemical Co.

The amine promoters, N,N-dimethyl-*p*-toluidine (DMPT; Albemarle Corporation) and N,N-dimethylaniline (DMA; Aldrich Chemical Co.) were used as received, XP-A amine promoter was made by Albemarle Corporation.

Methyl ethyl ketone peroxide (MEK-9) was supplied by Morac, Inc. Cobalt naphthenate (50% solution) was purchased from Aldrich Chemical Co. and diluted to 12% with mineral oil.

Procedures

Curing performances were studied at ambient and sub-ambient temperature by using a 10g sample mass in a 20ml glass bottle. Several 100g mass samples were also evaluated at room temperature in a 4-oz jar. A typical procedure is as follow: amine and cobalt solution were added into the resin, mixed then at desired temperatures for 1 min before adding MEKP, stirring continued and time was clocked until gel or cure was noted. For low temperature tests, resins were kept at the desired temperature for 15min before mixing with other ingredients. For 100g mass samples, we also recorded the exotherm of the formulation immediately after gel time was reached with a dual channel thermometer (Fisher Scientific).

Unsaturated polyester plaques were made by using two stainless steel plates laminated with 1/8 inch spacers. A blend of 80% Aropol 7221 and 20% styrene was used as the resin. The cure was accomplished at ambient temperature and the physical properties were measured after 10 days of curing. Shore D hardness was tested with a PCT hardness tester (Model 409, Type D). Impact resistance was performed on a Tinius Olsen pendulum impact tester; samples were notched and conditioned for 24hrs before testing. Tensile tests were conducted on a Sintech-1S machine at ambient temperature. Yellowness index was measured with a ColorQuest XE colorometer. Water and MEK absorption was performed at room temperature for 24 and 8 hrs, respectively.

Results and Discussion

XP-A is a colorless or slightly yellow liquid amine blend with very low viscosity. It can be easily mixed in any unsaturated polyester formulation. In order to understand the performances of this amine promoter, we performed a side-by-side comparison with commonly used promoters like DMPT and DMA. Compositions of formulations (in grams) evaluated in Figures 1—3 are listed in Table 1 and 2.

Table – 1 Formulations used in Figures 1 and 2

	A	B	C	D
Aropol 7221	9.935	9.930	9.920	9.910
Amine promoter	0.005	0.010	0.020	0.030
Cobalt naphthenate	0.050	0.050	0.050	0.050
Initiator	0.100	0.100	0.100	0.100

Table – 2 Formulations used in Figures 3

	A	B	C	D
Aropol 7221	9.983	9.980	9.977	9.975
Amine promoter	0.002	0.005	0.008	0.010
Cobalt naphthenate	0.015	0.015	0.015	0.015
Initiator	0.100	0.100	0.100	0.100

First let us look at the basic properties of XP-A in comparison with DMPT and DMA. The physical properties of these three promoters are listed in Table 3. All three of them are liquid. We can see that XP-A has less color, which is desirable in most products. It has higher boiling point and flash point, mild odor, thus is easier and safer to handle. It contains significantly less aromatic structure, which could indicate this material to be less toxic. From these aspects, we can say that XP-A has the inherent properties to be more user friendly than DMPT and DMA.

Now let us compare the curing properties of these three amines. First is the gel time behavior below ambient temperature. At Sub-ambient temperatures as shown in Figures 1-2, XP-A was faster than both DMPT and DMA. This result showed that XP-A is potentially a very good curing promoter for low temperature cure of unsaturated polyester resins.

Table – 3 Physical properties of promoters

	DMPT	DMA	XP-A
Appearance	Light yellow	Yellow to brown	Colorless to pale yellow
Boiling point, ^oC	211	193	257.6
Flash point, ^oC	83	63	110
Odor	mild	strong	mild
Aromatic content	56.21%	63.63%	7.06%

With the increase of curing temperature, the difference of gel time between XP-A and DMPT/DMA samples was narrowed and DMPT samples even showed faster gel process than XP-A in some of our experiments. Higher concentrations of initiator, cobalt salt and promoter also gave similar results

In order to make a more accurate comparison at ambient temperature, we reduced the concentration of cobalt salt and amine (compare Table 1 and 2). The results are shown in Figure 3. At this temperature it was also observed that XP-A has lower gel times than DMPT and DMA when the amine concentration was low. But at high concentration (0.1%) we do see DMPT was a little faster than XP-A while DMA remains the slowest one.

These results show that the relative curing speed of DMPT and XP-A varies with concentration of initiator system. At low concentration of initiators and promoters, XP-A is able to promote curing of resin more efficiently than DMPT. Lower temperature needs more initiators/promoters for DMPT to equal the speed of XP-A.

Another interesting phenomenon observed in our experiments was that the relative gel speed (gel time) between DMPT and XP-A, which varied with the sample size for the same formulation. For example, DMPT gelled faster with 100g mass samples (see Table 4), even though XP-A gelled faster at 10g mass samples, The possible reason might relate to the heat transfer and the sensitivity of amine to the temperature. It could be because DMPT is more sensitive to temperature than XP-A, and the heat transfer in a 100g sample is more difficult than in a 10g sample, the reaction heat is able to accelerate DMPT system more efficiently than XP-A and DMA systems.

From Table 4 we also notice that XP-A produces a lower exotherm temperature than DMPT. This lower exotherm could potentially make it easier in handling when making the composites and also possibly reduce the shrinkage of the material.

Table – 4 Curing properties of samples*

	DMPT	DMA	XP-A
Gel time, min	12.3	16.1	12.9
Peak exotherm, ^{o}C	183	167	165
Peak time, min	21.5	29.8	27.7
Resin clear time, min	22.6	30.7	29.1
Resin clear temperature	177	164	161

* Formulation used in this test was 100parts of Aropol 7221, 0.1 parts of cobalt naphthenate solution, 2 parts of initiator, and 0.05 parts of amine promoters

Properties of the cured samples derived from DMPT, DMA, and XP-A are listed in Table 5. Hardness and impact resistance of a sample are related to the crosslinking density of this material. Usually a higher hardness represents a better crosslinking or cure. Above a certain crosslinking density, for the same formulation, a brittle sample usually has higher crosslinking density. Data in Table 5 showed that XP-A sample has much higher hardness and lower impact resistance than DMPT and DMA samples, which implies XP-A gives better cure than DMPT and DMA. The tensile tests also showed that resins cured by XP-A had better performances than samples cured by DMPT and DMA.

Table – 5 Properties of cured resins*

	DMPT	DMA	XP-A
Shore D Hardness			
0 second	75.0	73.7	77.0
10 second	57.3	57.2	61.5
Impact resistance, ft-lbf/in	0.29	0.34	0.26
Color, yellowness index	14.06	11.84	11.54
Water absorption, 24hrs, %	0.016	0.017	0.015
MEK absorption, 8hrs, %	5.2	5.5	5.1
Modulus, $X10^{5}$ psi	3.64	3.63	3.90
Peak load, lb	609	629	699
Yield Stress, $X10^{3}$ psi	6.82	6.77	7.41
Elongation, %	3.2	3.3	3.4

*The resin contained 100 parts of a blend of 80% Aropol 7221 and 20% styrene, 1 part of initiator, 0.05 parts of cobalt naphthenate solution and 0.05 parts of amine promoter

Color of the cured resin is an importance concern in unsaturated polyester industry. Lower colored materials not only are more acceptable to customers, but also make the color match easier. In the three promoters compared in this paper, XP-A derived samples have the lowest color (see Table 5). It becomes more significant if there is any heat treatment. Our tests indicated that the color of XP-A derived samples had 40% less color (characterized by yellowness index) than DMPT and DMA derived samples after treated 24 hrs at $80^{o}C$. This performance will give XP-A an additional advantage to compete with other amines.

Since a lot of unsaturated polyester composites are used in household areas, we also tested the water and solvent resistance of the cured resin. As shown in Table 5, the XP-A derived sample has the best water and MEK resistance. These improved properties make XP-A more suitable than DMPT and DMA in household and other water/solvent contact applications.

Conclusions

In comparison with DMPT and DMA, XP-A exhibits a number of advantages:

- Lower color
- Faster gel time
- Low peak exotherm
- Better mechanical properties
- Better water and solvent resistance
- Improved safety
- Potentially decreased toxicity

XP-A is an alternative to DMA that showed improves performances of the products, which can extend the UPR business to new areas.

References

1. D. L. Nelson, "Unsaturated Polyester Resins," in *Reaction Polymers*, W. Gum, W. Riese, and H. Ulrich, Eds., Carl Hanser Verlag, Munich Viena New York Barcelona (1992).
2. D. Rosato, "Reinforced Plastics: Thermosets," in *Encyclopedia of Polymer Science and Engineering*, Vol. 14, p. 350, H.F. Mark, N.M Bikalis, C.G. Overberger, and G. Menges, Eds., John Wiley and Sons, New York (1988).
3. R.F. Storey, D. Sudhakar, and M. Hogue, *J. Appl. Poly. Sci.*, **32**, 4919 (1986).
4. M. Kinkelaar and J. L. Lee, *J. Appl. Poly. Sci.*, **45**, 37 (1992).
5. G. Ozeroglu, *Poly.—Plast. Techn. & Eng.*, **43**, 661 (2004).

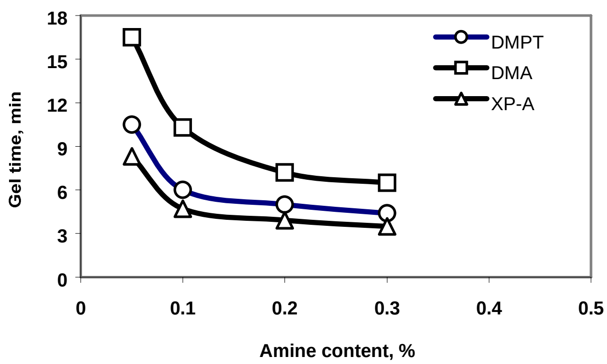

Figure – 1 Gel time at 15^{o}C

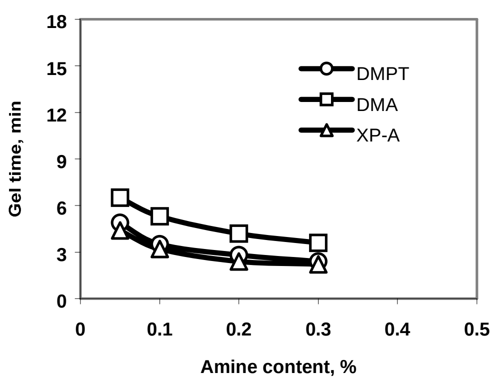

Figure – 2 Gel time at 20^{o}C

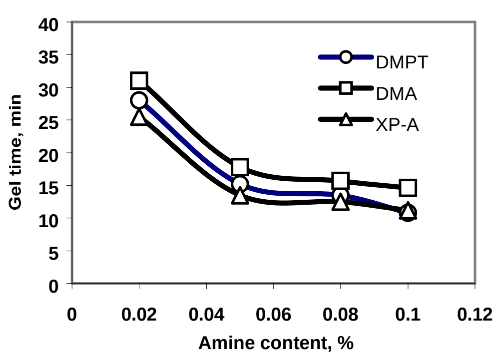

Figure – 3 Gel time at 25^{o}C with lower promoter concentration

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