

Melamine Formaldehyde Networks with Improved Chemical Resistance

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Introduction

Melamine formaldehyde resins (MFR) are used to crosslink many industrially applied coatings. Much of the MFR used in the US. are of the hexa(methoxymethyl)melamine (HMMM) type. As reaction partners for HMMM predominantly hydroxyl or carboxyl functional resins are used. The reaction of HMMM with hydroxyl polymers is generally well understood. The reaction is specific acid catalyzed with strong acid catalysts such as sulfonic acid commonly used. The acetal linkage formed can hydrolyze under acidic conditions leading to a loss of the network structure and attack on the film. Typical acid rain conditions are sufficient to damage the coating. This hydrolysis reaction is accelerated at higher temperature and increased humidity. One additional factor in the hydrolysis reaction of melamine crosslinked films is the basicity of melamine which leads to the absorption of acid in the film. The acid sensitivity of melamine crosslinked coatings has become more of a problem with the introduction of high solids coatings which require higher levels of melamine resin.¹ In the automotive topcoat area this problem is especially severe. Where many attempts have been made to replace melamine crosslinking with other crosslinker. From a cost and performance standpoint melamine crosslinker are very attractive, providing much of an incentive to find ways to improve the acid resistance.

The self-condensation reaction of melamine resins² during overbake conditions and the ensuing embrittlement is also a result of hydrolytic instability of the crosslinks, leading to a loss of crosslinking and the formation of a self-crosslinked network. A more stable link of the polymer with the melamine resin should also reduce the loss of flexibility of melamine crosslinked coatings on overbake.

Melamine formaldehyde chemistry offers many other alternative ways of crosslinking besides reacting with hydroxyl and carboxyl groups, HMMM can react with NH and CH reactive sites on polymers to form linkages which are potentially more resistant to hydrolysis.

APPROACHES TO IMPROVED STABILITY OF NETWORK

Reduced Melamine Resin Level and Dual Cure Systems

Blocked Isocyanates

Ketoxime³

Malonate⁴

Siloxane⁵

Epoxy⁶

More Stable Crosslinks

NH crosslinks

Primary Carbamate^{7, 8}

Amide

Urea

CH crosslinks

Phenolic⁹

Malonate blocked isocyanate¹⁰ and Acetoacetate

SH functional.¹¹

Hydrophobic Backbone or Improved Hydrolytically Stable Backbone

Ester free backbone¹²

Polyurethane with hydrophobic groups¹³
Acrylic polymers¹⁴

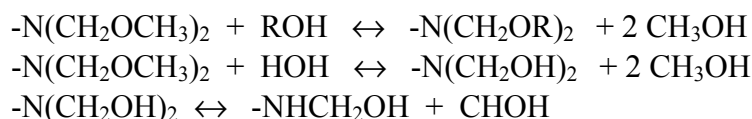
Other potential approaches

Reduced solubility of melamine¹⁵
Reduced basicity of melamine
Combination with other amino resins
Change in hydrolysis equilibrium

Reaction of HMMM with Functional Groups

Hydroxyl Groups

The reaction of HMMM with hydroxyl functional polymers has been studied extensively. HMMM reacts readily with hydroxyl functional compounds in the presence of an acid catalyst. This exchange reaction proceeds at room temperature. The rate of reaction is a function of the pH of the system. Reaction with water also proceeds leading to a hydrolysis of the crosslinked network. Although this reaction is reversible, subsequent demethylation and loss of formaldehyde leads to a permanent loss of crosslinks¹⁶. The hydrolysis reaction can also be accelerated in the presence of UV radiation.¹⁷



Reduced Melamine Resin Level and Dual Cure System

It has been found that coating systems which utilize less than 25 % of melamine resin generally give acceptable acid resistance and exterior durability¹⁸. For the high solids polymer systems used in the US, however this level of melamine resin is not sufficient to achieve the required nonvolatile content. Yet increasing the melamine content has a negative impact on acid etch resistance. Every conceivable reaction mechanism has been studied as a means to improve this deficiency. Some of these approaches are being used to improve the resistance properties of melamine crosslinked films.

Stability of the Methylene or Methylene Ether Linkage

Comparison of the stability of methylene bridges of different amino compounds shows that the stability is related to the basicity of the nitrogen. An increase in basicity of either nitrogen leads to a decrease in stability of the bond. The N-C linkage in methylene ether bonds (-NHCH₂OR) was found 1000 times more stable¹⁹ than the ether bond under acidic pH conditions. Conclusions about the stability of the methylene linkage can be drawn from the published literature on the reactions and stability of phenol, amide, urea and imidazolidinone formaldehyde derivatives.

Stability of the >N-CH₂-N< Linkage

Methylene derivatives are arranged in order of increased stability.²⁰

Alkyl-NH-CH ₂ -N<(R) ₂	Cyclic structure improved stability
Triazine-NH-CH ₂ -N<(R) ₂	sec.-Amine
-CONH-CH ₂ -N<(R) ₂	sec.-Amine
-CONH -CH ₂ -NH-OCR	Amide
Triazine-NH-CH ₂ -NH- Triazine	Melamine
Triazine-NH-CH ₂ -NHCOOR	Carbamate
Triazine-NH-CH ₂ -NH-CO-R	Amide

Glycoluril -CH₂- Glycoluril Glycoluril

The stability of the >N-CH₂-N< linkage increases with a decrease in the basicity of the nitrogen. Simple reaction products of formaldehyde with primary amines are only stable in the trimeric form. Melamine formaldehyde Mannich base reaction products with secondary amines will form by simple blending the components and will react at low temperature even in the absence of a catalyst. Mannich bases of the less basic amide with a sec. amine gives improved stability compared to the melamine compound.

The bis-amide structures are reported to be reactive at a pH of <3.0. Melamine-carbamate and also melamine-amide products provide further improvement in resistance properties in an acid environment. Both self-condensed glycoluril and melamine reaction products offer even further increase in acid resistance.

CH- Crosslinks

Malonate blocked NCO²¹



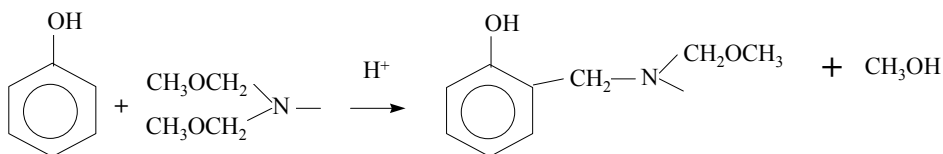
The CH groups in malonate blocked isocyanates react readily at 120°C with HMMM in the presence of a strong acid catalyst. NMR analysis confirms the presence of this crosslink. Acid resistance of this dual (malonate bl. NCO/OH/HMMM) crosslinked network is superior to a OH/HMMM network.

Acetoacetate



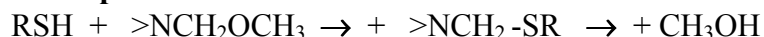
Acetoacetates and isocyanates blocked with acetoacetates also react with HMMM, but the reaction speed is slower and a cure temperature of 140°C is required for adequate cure. The increased stability²² of the linkage assures less embrittlement on overbake and better acid resistance.

Phenol



Ring alkylation of phenols can either occur in the ortho or para position. This reaction produces extremely stable links which are being used in modified phenolic end group terminated epoxy resins in combination with HMMM to give improved chemical resistance. This reaction also permits the synthesis of carboxyl functional melamine resins²³ by reacting salicylic acid with HMMM.

Mercaptan



Reaction of HMMM with mercaptan presents an elegant way to determine the reaction mechanism of melamine resins. The mercapto linkage cannot be reprotonated and therefore the reaction does not reverse. A potential advantage in this reaction is a lower cure temperature and improved resistance properties.

Hydrophobic Backbone or Hydrolytically Stable Backbone

Several approaches have been taken to improve the resistance properties of melamine crosslinked films by increasing the steric hindrance of the ether linkage or reducing the amount of ester linkages and replacing these linkages with hydrolytically more stable urethane bonds. Although the sec. carbamate groups in urethanes are potentially reactive with melamine resins, no publications have specifically discussed this subject. The presence of hydrophobic side chains in polyurethanes has a significant effect on the acid resistance in the film. Indications are that the

large differences in solubility parameter between hydrophobic side chains and the urethane backbone causes phase separation and an enrichment of the hydrophobic chains on the surface, decreasing the wetting of the surface thereby increasing the acid resistance.

Other Approaches

Surface analysis of crosslinked coatings exposed to acid rain show surface leaching of melamine and pitting to be the primary mode of deterioration. The probable mechanism is presumably the hydrolysis of the ether bonds between polymer and melamine resin, leading to clusters of melamine self-condensate on the surface, which in time will further degrade or leach from the surface. One publication claims further hydrolysis of melamine to ammeline and ammelide²⁴. This mechanism might apply to laboratory studies, but it is questionable under natural exposure conditions if the solubility of melamine might not dominate the surface loss. The basic nature of melamine crosslinked films permits the formation of acid / base complexes with reduced water solubility.

One of the factors contributing to the acid sensitivity problem of melamine crosslinked coatings is the basic nature of melamine. Melamine has a pKa value of 8.95. Substituted melamine derivatives with an increase basicity have shown as expected improved cure response but poorer resistance properties.

Improvement in acid resistance should also be possible by combining melamine chemistry with other amino aldehyde compounds with reduced basicity. This approach could reduce not only the basicity of the film but would also permit the built up of an amino self-condensed networks with better resistance properties. Imidazolidinone derivatives are one of the prime candidates for such a modification.

Recently carbamate functional formaldehyde free triazine derivative have been introduced into the market²⁵. These materials perform similar to activated ester in crosslinking hydroxyl functional polymers.

Conclusions

The versatility of melamine chemistry is only now starting to be explored. A driving force is the required improvements in acid resistance for automotive topcoats. One of the approaches taken is the improvement in acid resistance which can be achieved by deviating from the typical ether crosslinks obtained with hydroxyl functional polymers. Other approaches are the combination of melamine crosslink chemistry with other crosslinking mechanism.

Modification of the melamine molecule to reduce basicity of the nitrogen holds some promise as does the elimination of formaldehyde chemistry all together.

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