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(Baxxodur[®] EC 210)**

**A Hardener for Epoxy Systems with
Superior Carbamate Stability**

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A Hardener for Epoxy Systems with Superior Carbamate Stability

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Abstract

Epoxy-based industrial maintenance coatings offer excellent chemical and mechanical performance. However, the amine type hardeners often employed can easily react with atmospheric carbon dioxide and moisture to form carbamate salts. These carbamate salts accumulate on the surface and cause blush and intercoat adhesion issues. Adducts based on methylcyclohexyl diamine (MCDA, Baxxodur[®] EC 210), a cycloaliphatic diamine curative for epoxy resin systems, displayed enhanced carbamate stability compared to adducts based on both isophorone diamine (IPDA) and m-xylylene diamine (MXDA). This behaviour was further validated in coating tests, where coating formulations based on MCDA exhibited superior gloss. The cure behavior, mechanical properties, and thermal properties of MCDA, IPDA, and MXDA cured systems were also assessed using various analytical techniques such as differential scanning calorimetry and rheology. Overall, MCDA was proven to be an attractive building block for epoxy diamine, industrial coating systems.

Introduction

The aim of industrial maintenance coatings is to protect surfaces such as concrete from degradation in aggressive environments. Due to their good adhesion, high mechanical and thermal properties, and good chemical resistance, epoxy-based systems are well suited for this task.^{1,2} Epoxy resins can be hardened with a variety of co reactants, such as amines, phenols, thiols, and carboxylic acids, leading to a wide range of handling and performance profiles. Cycloaliphatic diamine hardeners are used extensively in flooring applications³ because they offer a balance between ease of handling and final properties such as fast cure, low viscosity, low toxicity, good adhesion, and excellent color stability. Furthermore, cycloaliphatic diamines are particularly well suited to low temperature

cure or where adhesion to wet concrete is required.^{3,4}

In flooring applications, amines are often used in adduct form, where excess amine is pre reacted with epoxy resin. In general, adducts are less prone to blushing because the relative primary amine content has been reduced in the molecule, with the resulting adducts having reduced hygroscopicity.^{2,4} Blushing is caused by the formation of carbamate salts, which form when primary amines react with atmospheric carbon dioxide and water. In addition to blush reduction, amine adducts are also less corrosive and less volatile. These advantages come at a cost, however, as adduction leads to a significant increase in viscosity. To lower viscosity, amine adducts are often formulated with solvents or plasticizers such as benzyl alcohol (BnOH), which, in addition to serving as a viscosity reducer, can also accelerate the epoxy-amine reaction at ambient or sub-ambient temperatures.^{3,4}

Methylcyclohexyl diamine (MCDA), is a cycloaliphatic diamine epoxy hardener, and, like isophorone diamine (IPDA),³ is well suited to flooring applications; MCDA has a lower viscosity than IPDA, which is also well known for its low viscosity.⁵ MCDA consists of two regioisomers, 2,4 and 2,6-MCDA, with four and three stereoisomers, respectively (Figure 1).⁶ Both IPDA and MCDA readily react with epoxy resins under ambient or sub ambient temperatures, and their low viscosities allow for greater freedom in formulation and/or extended working pot-life.

Herein we explore the differences between adducts of two cycloaliphatic diamines, IPDA and MCDA, and between adducts of MCDA and an aryl diamine, m-xylylene diamine (MXDA). All three amines offer advantages and disadvantages in terms of their curing profile, thermal profile, and appearance. The diamine type hardeners used in this study are shown in Figure 1.

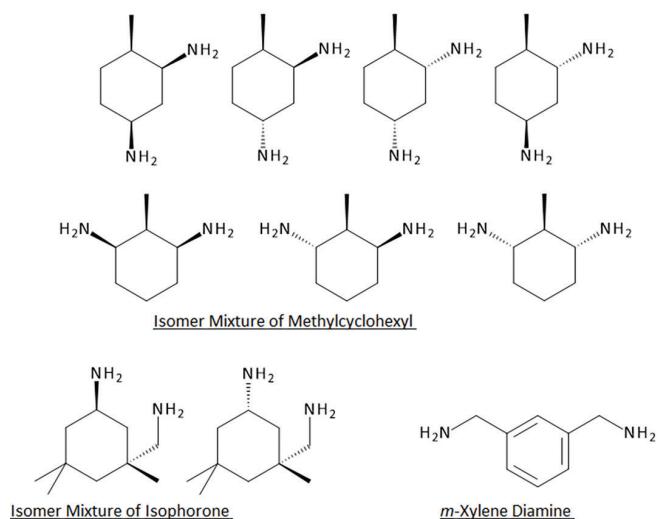


Figure 1. Diamine-type epoxy hardeners employed in this study.

Experimental

Materials

Diglycidyl ether of bisphenol-A (DGEBA) was obtained from Leuna-Harze GmbH (Epilox® A 19-03, epoxy equivalent weight 184 g/mol). Isophorone diamine (Baxxodur® EC 201, amine hardener equivalent weight 42.6 g/mol) and methylcyclohexyl diamine (Baxxodur® EC 210, amine hardener equivalent weight 32 g/mol) were obtained from BASF SE. m-Xylene diamine (amine hardener equivalent weight 34 g/mol) was purchased from Mitsubishi Gas Chemical.

Benzyl alcohol was purchased from Honeywell. All chemicals were used as received.

Adduct Synthesis

Amine functional adducts (Figure 2) were synthesized with excess amine. The molar ratio of DGEBA to diamine was either 1:16, 1:8, or 1:2.5. For adducts with a molar ratio of 1:2.5, BnOH was added to keep viscosity within a workable range. For these adducts, BnOH and diamine were employed in equivalent amounts (wt%). The synthesis of 1:2.5 (DGEBA/MCDA) adduct is shown as an example. MCDA (175 g, 1.37 mol) and BnOH (175 g) were combined in a 1 L round bottom flask under a nitrogen atmosphere. DGEBA (200 g, 0.55 mol) was added dropwise and the mixture was stirred to facilitate complete reaction. No active heating was employed, although the temperature of the reacting mass was kept below 100 °C.

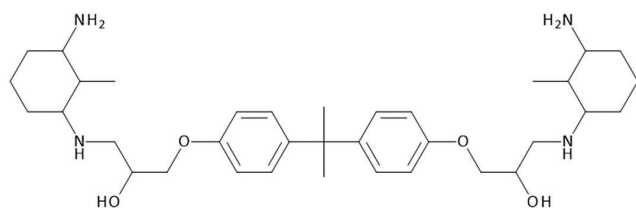


Figure 2. Idealized MCDA-based adduct.

Preparation of Reactive DEGBA-Adduct Mixtures

To harden DGEBA with the prepared adducts or adduct-BnOH mixtures, reactive mixtures were formulated using a 1:1 stoichiometric ratio of epoxy groups to active NH functionality.

The epoxy adduct or epoxy adduct-BnOH mixtures were stirred via a propeller mixer at 2,000 rpm for 1 min. Immediately following preparation, differential scanning calorimetry (DSC) and rheological experiments were conducted, and samples for Shore D and spectral gloss measurements were prepared.

Methods

DSC (204 F1 Phoenix, Netzsch) was used to determine the reaction and thermal profile [onset temperature (T_o), peak temperature (T_p), glass transition temperature (T_g)] according to ASTM D3418 using a heating rate of 20 °C/min starting with ambient temperature (23 °C).

The rheological profiles (pot-life and gel time) at 23 °C and 75 °C were determined using a conventional shear stress controlled plate-plate rheometer (MCR 301, Anton Paar) with a plate diameter of 15 mm and a gap distance of 0.25 mm, using rotational mode (pot-life) or oscillatory forces (gel time). Pot-life was measured as the time at a given temperature needed to attain a viscosity of 10,000 mPas. Gel point was defined as the crossover point of the storage and loss moduli and gel time was defined as the time taken from addition of the hardener to the reaction mixture, to reach the gel point.

Shore D measurements were conducted by pouring 3 g of a reactive mixture into an aluminum pan with an inner diameter of 30 mm. The systems were cured under two different atmospheric conditions, either 10 °C (65% relative humidity) or 23 °C (ambient atmosphere). Shore D hardness measurements were conducted every hour according to DIN ISO 7619 1 on test specimens with a thickness of 35 - 36 mm.

Ease of carbamate formation was visually monitored by placing 3 g of adduct, or adduct BnOH mixtures, in 35 mm diameter wells of a 2 x 3 well plate. The adducts and adduct-BnOH mixtures were then stored at 23 °C and 50% relative humidity for 48 hours, and photographs were taken after 2, 4, 6, 8, 16, 24, and 48 hours. Carbamates were detected through the visual observation of white precipitate or surface irregularities.

Gloss tests were conducted by applying the reactive epoxy adduct-BnOH mixtures to a matt black surface with a 500 µm doctor blade. Curing the coatings at 8 °C for 69 hours yielded hardened films. Specular gloss was measured with a micro-TRI (20°, 60°, 85°) gloss meter from Byk Gardner with a 20° geometry according to ASTM D523.

Results and Discussion

Adduct Production

A total of nine adducts were synthesized by slowly adding DGEBA to excess amine (Table 1). The adducts were not

Table 1. Summary of adducts and adduct-BnOH mixtures.

Adduct	Mixing Ratio (DGEBA: Diamine)	DEGBA (g)	Diamine (g)	BnOH (g)
MCDA-A16	1:16	100	556	-
IPDA-A16	1:16	100	740	-
MXDA-A16	1:16	100	591	-
MCDA-A8	1:8	100	278	-
IPDA-A8	1:8	100	370	-
MXDA-A8	1:8	100	296	-
MCDA-A2.5-BnOH	1:2.5	200	175	175
IPDA-A2.5-BnOH	1:2.5	200	234	234
MXDA-A2.5-BnOH	1:2.5	187	175	175

isolated or purified following synthesis; all systems synthesized are mixtures of DGEBA-diamine adducts and residual diamine. The use of BnOH allowed epoxy-diamine mixing ratios as low as 1:2.5 for all three diamines. Without the use of solvent the lowest mixing ratio achievable was 1:8.

Thermal Properties

When employing a stoichiometric mixing ratio in the absence of BnOH, adduction of MCDA, IPDA, and MXDA led to a slight decrease in the onset and peak exotherm temperature, and a slight increase in T_g , as compared to the pure diamines. Both MCDA and IPDA are cycloaliphatic amines containing two primary amines, resulting in similar polymeric backbone structures and T_g s. Compared to MXDA, a methyl group separates the amine groups from the aromatic core, leading to more backbone flexibility and a lower T_g . As expected, the adducts employing BnOH saw a reduction in T_g by 40 - 70 °C. The

Table 2. Thermal properties of DGEBA hardened with adducts and adduct-BnOH mixtures.

Adduct	Onset (°C)	Peak (°C)	T_g (°C)
MCDA	77	108	168
IPDA	73	103	159
MXDA	75	101	124
MCDA-A16	74	105	170
IPDA-A16	72	101	164
MXDA-A16	72	99	126
MCDA-A8	71	104	171
IPDA-A8	69	100	163
MXDA-A8	69	98	127
MCDA-A2.5-BnOH	57	94	98
IPDA-A2.5-BnOH	49	87	94
MXDA-A2.5-BnOH	53	89	86

DSC results are summarized in Table 2. All DSC values reported here for the pure diamines are in good agreement with those previously reported.⁵⁻⁸

Rheological Properties

Greater differences were observed when comparing the rheological profile of DGEBA cured with MCDA-adducts versus IPDA-adducts or MXDA-adducts. For example, MXDA-A16 formulated with DGEBA had the lowest viscosity, followed by MCDA-A16, and then IPDA-A16, at room temperature (Table 3). At an elevated temperature of 75 °C, MCDA-A16 formulated with DGEBA displayed the lowest viscosity while the viscosities of formulated MXDA-A16 and IPDA A16 adducts were very similar to one another. Additionally, the viscosity behavior of DGEBA formulations with the various adducts was found to differ. For example, as shown in Figure 3, although formulations employing MCDA-A16 had a higher initial viscosity than those with MXDA A16, the formulated viscosity of the MCDA-A16 progressed more slowly, yielding a longer pot-life. Pot life is influenced by a combination of two factors, the starting viscosity and the rate of reaction, and even though MXDA-A16 has a lower starting viscosity, it reacts more quickly than MCDA A16. This trend is also visible in the time to gel, where formulated MXDA-A16 was found to reach gel point in the shortest amount of time, followed by IPDA-A16 and then MCDA-A16. As all A16 adducts theoretically have the same functionality, therefore MXDA's fast gel time is indicative of its faster reaction rate.

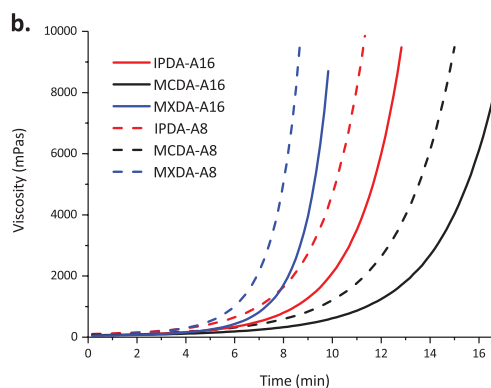
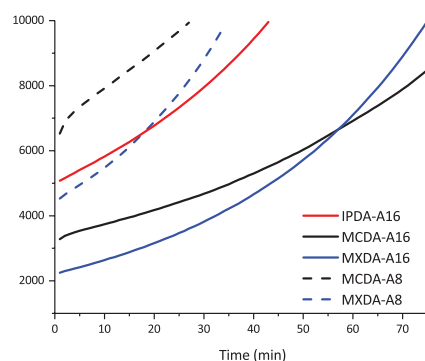


Figure 3. Viscosity development of DGEBA hardened with the various adducts and adduct-BnOH mixtures, at a) 23 °C and b) 75 °C. Viscosity data for DGEBA hardened with IPDA-A8 is not reported because the starting viscosity of this formulation exceeded 10,000 mPas.

Table 3. Rheological properties of DGEBA hardened with adducts and adduct-BnOH mixtures.

Adduct	Initial Viscosity (mPas)	Pot Life (min)	Gel Time (min)	23 °C		75 °C	
				Initial Viscosity (mPas)	Pot Life (min)	Gel Time (min)	Initial Viscosity (mPas)
MCDA-A16	3,460	86	633	108	17	41	
IPDA-A16	5,280	43	421	149	13	37	
MXDA-A16	2,360	75	333	146	10	21	
MCDA-A8	7,130	27	561	167	15	41	
IPDA-A8	> 10,000	NA	396	263	11	33	
MXDA-A8	4,800	34	257	269	9	19	
MCDA-A2.5-BnOH	> 10,000	NA	536v	281	10	20	
IPDA-A2.5-BnOH	> 10,000	NA	481	358	9	18	
MXDA-A2.5-BnOH	> 10,000	NA	227	340	5	6	

Shore D Development

The progression of Shore D hardness over time was determined for the synthesized adducts in combination with DGEBA, under two different atmospheric conditions, either 10 °C (65% relative humidity) or 23 °C (ambient atmosphere). Shore D development is also dependent on two factors: rate of network density build-up and polymeric backbone stiffness. Here, we are comparing diamines with similar rigidity and functionality, so differences in Shore D development will be dependent primarily on the reaction rate. Unsurprisingly, adducts based on MXDA were found to reach a Shore D over 80 significantly earlier than adducts based either on IPDA or MCDA (Table 4, Figure 4). IPDA was found to have a slightly better performance than MCDA at 10 °C, both in terms of hardness development and tack-free

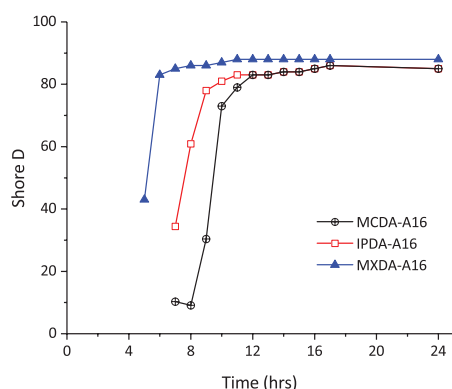


Figure 4. Shore D development over time of DGEBA hardened with MCDA-A16, IPDA A16, and MXDA-A16 adducts at 23 °C (ambient atmosphere).

Table 4. Shore D and tack development of DGEBA hardened with adducts and adduct-BnOH mixtures.

Adduct	Shore D > 80 (hours)	Tack-free Time (hours)	Shore D > 80 (hours)	Tack-free Time (hours)
	10 °C, 65% RH		23 °C	
MCDA-A16	38	> 48	12	12
IPDA-A16	32	13	10	7
MXDA-A16	20	12	6	6
MCDA-A2.5-BnOH	80	11	16	4
IPDA-A2.5-BnOH	77	7	17	4
MXDA-A2.5-BnOH	28	6	6	2

time, but IPDA and MCDA adducts displayed equivalent behavior when the temperature was raised to 23 °C.

Carbamate Stability

Primary amines react readily with atmospheric carbon dioxide and water vapor to form carbamate salts. These salts tend to accumulate on the surface of the reacting mass, which leads to blushing. Blushing can have detrimental effects on gloss, color, and intercoat adhesion.^{3,4} Stability against carbamate formation of the various adducts was determined using two different approaches. First, pure adducts or adduct-BnOH mixtures in the absence of DGEBA, were aged in a climate chamber at 23 °C and 50% RH. Formation of carbamate salts was then detected visually, through the observation of white precipitate or surface irregularities (Figure 5).

A significant amount of carbamate salt was visually present in MXDA-A16 after only two hours and in IPDA-A16 after 16 hours. Comparatively, although MCDA A16 turned slightly turbid after 16 hours, no carbamate precipitate was visible in MCDA 16 even after 48 hours. Adducts containing BnOH were also tested. Again, carbamates were first detected in MXDA-A2.5-BnOH after 8 hours, then in IPDA-A2.5-BnOH after 24 hours, and no turbidity or carbamates were visible in MCDA-A2.5-BnOH after 48 hours. However, it is important to note that the A2.5-BnOH adducts had significantly less, visible carbamate salts than their A16 counterparts. This is due to the decreased primary amine content of the A2.5-BnOH adducts, as well as the presence of

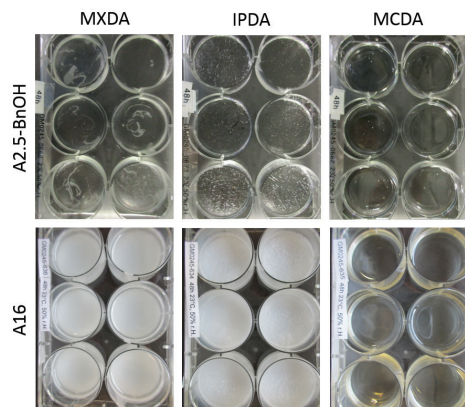


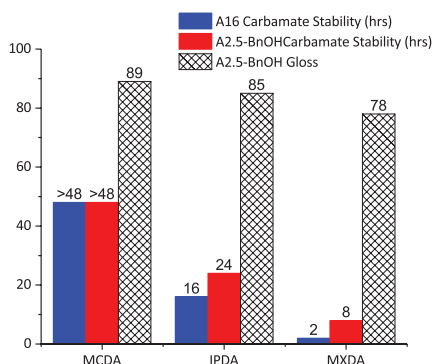
Figure 5. Adducts and adduct-BnOH mixtures aged at 23 °C and 50% relative humidity for 48 hours. The presence of carbamates was detected visually through the observation of white precipitate or surface irregularities, as was the case for IPDA-A2.5-BnOH.

BnOH, which serves to further dilute the primary amine concentration. As noted earlier, carbamate formation can be particularly detrimental to gloss. Therefore, our second approach to carbamate detection was to measure spectral gloss after complete curing at 8 °C and 70% RH. These low temperatures and high humidity conditions serve to accelerate carbamate formation. Reactive formulations employing the 2.5 BnOH adducts were coated onto a matt black surface, and gloss readings were determined at 20° following cure. A similar carbamate stability trend was observed; MCDA A2.5 BnOH had the highest gloss reading of 89, indicating the lowest level of carbamate formation on the coating surface, followed by IPDA-A2.5-BnOH with 85, and then MXDA A2.5 BnOH with 78. This trend clearly demonstrates that qualitative detection of carbamate salt formation can manifest itself in more quantitative application testing, such as spectral gloss readings (Figure 6).

Conclusions

Epoxy-amine adducts based on MCDA (Baxxodur® EC 210) were readily synthesized, with DGEBA-diamine adduct ratios ranging from 1:16 to 1:2.5. For the 1:2.5 adducts, BnOH was used as a solvent to help mediate the resulting high viscosities. MCDA-based adducts were found to react significantly slower than MXDA-based adducts, but the reactivity of MCDA-based adducts

Figure 6. Carbamate stability of pure adducts and adduct-BnOH mixtures aged at 23 °C and 50% relative humidity, and spectral gloss readings of DGEBA hardened with A2.5-BnOH adducts at 8 °C and 70% relative humidity.



were comparable to IPDA-based adducts. The reactive formulations tested were very simple, and did not include co-hardeners or accelerators. Proper selection of co-hardener(s), accelerators, plasticizers, and solvents can be used to further fine tune the reaction kinetics to match desired applications. Additionally, although MCDA-based adducts had higher initial formulation viscosities than the MXDA-based adducts, the viscosity of MCDA-based adducts progressed more slowly, leading to a longer pot-life. A long pot-life, where prolonged low viscosity allows for easy handling, is crucial to the production of defect free, high-quality coatings. Lower formulated viscosity also allows for greater formulation freedom; for example, solvent content can be reduced and other high viscosity or solid components can be more easily incorporated. Most importantly, MCDA-based adducts were found to have greater stability against carbamate formation relative to the MXDA- and IPDA-based adducts. This behavior was further validated in coating tests, where a formulation employing MCDA-based adducts resulted in a coating with the highest spectral gloss; carbamate formation is detrimental not only to spectral gloss, but also to yellowing and intercoat adhesion. Overall, MCDA is an attractive building block for epoxy-diamine systems and is particularly well suited to industrial coatings applications.

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