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Epoxy adhesive formulations using latent imidazole metal cation complexes

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Complexes of 2-methylimidazole with cations from several metal sulfates were prepared and investigated as curing agents for epoxy resins. The reactivity of one-part formulations of these complexes with a bisphenol A type epoxy resin was determined by the differential scanning calorimetry and the pot life observed by viscosity measurements. Tensile lap shear tests at room temperature and at 120°C were used to evaluate the adhesive strength of the formulations directly after preparation as well as after one and three months of storage at room temperature.

The DSC measurements showed much lower reactivity (7 – 32%) and higher reaction temperatures of the complex formulations in comparison to the mixtures with pure 2-methylimidazole. The viscosity of most formulations remained almost unchanged over the observed period of three months. The adhesive strength of the freshly prepared complex formulations is comparable to a formulation with pure 2-methylimidazole and decreases over time, depending on the type of metal cation and the cation-to-imidazole molar ratio. The obtained results indicate that complexes of 2-methylimidazole with cations are suitable as latent curing agents for epoxy resins.

Keywords: epoxy adhesives, latent curing agent, imidazole complexes, pot life, shear strength.

INTRODUCTION

This work describes a one-part epoxy resin compositions with imidazole complexes as latent curing agents[1–3]. Epoxy resin compositions for use as adhesives or molding materials can be formulated as two-part systems, wherein the resin component and the curing agent are prepared separately and must be mixed before application, or as the one-part systems which are ready-to-use mixtures of a resin with a suitable curing agent. Since the components of the two-part systems must be accurately measured and mixed before application, measurement errors are likely to occur which can lead to faulty adhesive joints. Also, the quick reaction between the resin and the curing agent does not allow for the extended storage of the mixed adhesive. The one-part systems do not suffer from the measurement errors mentioned above. However, premature commencement of the reaction between the epoxy resin and the curing agent may still lead to a reduction in storage stability. The most common solution to this problem are epoxy resin formulations with dicyandiamide as a curing agent which are known for long storage stability, but resin compositions with imidazoles and their complexes are used as well[1, 4–7]. In this work we present the properties of epoxy adhesives hardened with imidazole complexes[1], which were obtained by the new method of synthesis and purification of these products[4–7]. Authors developed a new way to obtain the latent curing agents on the basis of imidazole and inorganic metals salts, which will be published as new patent application.

MATERIALS AND METHODS

Six imidazole complexes with imidazole-to-metal-cation molar ratios of 2:1 and 4:1 were obtained in water from 2-methylimidazole (2MI) and appropriate salt: copper(II) sulfate(VI) $CuSO_4 \cdot 5H_2O$, nickel(II) sulfate(VI) $NiSO_4 \cdot 7H_2O$ and cobalt(II) sulfate(VI) $CoSO_4 \cdot 7H_2O$ (products of Sigma-Aldrich). The precipitates obtained (6 coloured products) were separated and purified by means of acetone. The purified products were dried, and then ground to fine powders.

The compositions of adhesives were obtained using a bisphenol A epoxy resin Epidian 6 from Organika Sarzyna S.A. in Nowa Sarzyna/Poland), and mixing it with an appropriate quantity of each imidazole complex such that 5 g of pure 2-methylimidazole were added to 100 g of epoxy resin. Table 1 lists the synthesized complexes, their acronyms, the amount added to 100 g of resin and the resulting colour of the composition. A mixture of 5 g 2-methylimidazole in 100 g of epoxy resin was used as a reference formulation.

Pot life was characterized by measuring the viscosity (defined to viscosity values 100 Pa·s) of epoxy compositions during the storage time at room temperature (23 – 25°C) by means of an ARES Rheometer (from Rheometric Scientific), over a 600 s time frame, in parallel-plate 25 mm configuration with a gap of 1 mm.

The curing process of the epoxy adhesives was characterized using a differential scanning calorimeter DSC Q-100 by the TA Instruments (USA), at a heating rate of 10°C/min in the temperature range of 30 – 300°C and glass transition was determined using of DSC during second run, at a heating rate of 10°C/min in the temperature range of 30 – 250°C.

Adhesive joints of the epoxy compositions for lap shear tests were prepared on aluminium "Duralumin PA6" (AlCu4MgSi) after surface preparation according to the Polish standard PN-69/C-89300 (mechanical abrasion, cleaning in acetone and chromatic etching). The epoxy compositions were cured for 4 hours at 140° C. The determination of tensile shear strength was conducted by means of an Instron material testing machine at a crosshead rate of 5 mm/min in accordance with standard PN-ISO 4587.

Table 1. The presentation of Imidazole Complexes and Epoxy Adhesives

Theoretical chemical constitution	Acronym of imidazole complex	Molar mass of the complexes [g/mol]	Content of imidazole [%]	Amount of imidazole complex per 100 g of epoxy resin Epidian 6 [g]	Color
$Cu(2MI)_2SO_4$	Cu2MI	323.5	50.70	9.85	turquoise
$Ni(2MI)_2SO_4$	Ni2MI	319.0	51.41	9.70	green
$Co(2MI)_2SO_4$	Co2MI	319.0	51.41	9.70	violet
$Cu(2MI)_4SO_4$	Cu4MI	487.5	67.28	7.42	dark blue
$Ni(2MI)_4SO_4$	Ni4MI	483.0	67.91	7.35	dark green
$Co(2MI)_4SO_4$	Co4MI	483.0	67.91	7.35	violet

RESULTS

Table 2 and figure 1 show the results of viscosity measurements during the observed time frame of 3 months in comparison to the reference formulation.

The pot life of epoxy adhesives with imidazole complexes stored at room temperature is longer than 90 days (3 months) and 30 times longer than the reference composition with 2-methylimidazole. The biggest change of viscosity is observed for the adhesive based on Co4MI, showing a three-fold increase.

Table 3 presents the results of the investigation of the curing process of the epoxy adhesives by DSC in comparison to the reference formulation.

The reference formulation with pure 2-methylimidazole yields the highest reaction enthalpy with 302 J/g, and the reaction enthalpy of all the investigated imidazol complex formulations is significantly lower in the range from 23 to 99 J/g or 7 to 32% of the reference value. The peak temperature of the curing reaction increases rapidly from 123°C for the reference formulation to the values in the range from 147 to 175 °C for the complex formulations.

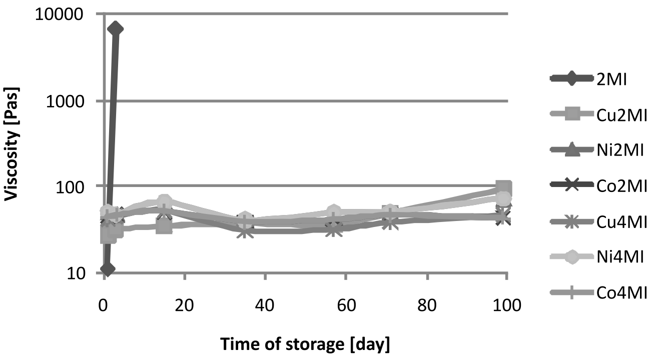

Figure 1. The viscosities of Epoxy Adhesives on the Selected Days of Storage

Table 3. The results of the Curing Process Investigations of Epoxy Adhesives

Acronym of curing agent	Enthalpy [J/g]	Tmax [°C]	Glass transitions [°C]
2MI	302.00	123.00	124.3
Cu2MI	62.94	174.86	66.8
Ni2MI	32.41	146.72	104.9
Co2MI	22.67	150.05	120.3
Cu4MI	98.67	164.96	106.5
Ni4MI	39.08	149.94	117.9
Co4MI	39.10	154.91	112.4

Small reaction enthalpies and high peak temperatures of the curing process for epoxy adhesives hardened with imidazole complexes lead to the conclusion that these complexes are latent curing agents for epoxy resin.

Table 4 and figure 2 present the results of tensile shear strength tests (at room temperature) for aluminum joints with the epoxy adhesives obtained directly after mixing the composition and after one and three months of storage.

The shear strengths for epoxy adhesives hardened with imidazole complexes are comparable to the shear strength of the reference formulation. The best value of this parameter is obtained using the imidazole complex with copper (II) in the molar ratio of 2:1 (Cu2MI). The shear strengths obtained using the complexes with a molar ratio imidazole:metal cation 2:1 are generally bigger than those for the 4:1 complexes.

Table 5 and figure 3 present the results of shear strength (at 120°C) for aluminum joints with the epoxy adhesives

Table 2. The viscosities [Pas] of Epoxy Adhesives on the Selected Days of Storage

Acronym of curing agent	Time of storage [days]						
	0	2	14	34	56	70	98
2MI	11.18 ±0.33	6741.25 ±277.30	–	–	–	–	–
Cu2MI	27.45 ±2.62	31.52 ±2.25	34.76 ±0.36	37.14 ±1.45	35.82 ±0.37	48.44 ±2.04	93.01 ±0.92
Ni2MI	50.90 ±2.91	47.51 ±0.68	66.02 ±0.44	41.02 ±0.46	50.02 ±0.34	50.49 ±0.34	72.75 ±0.35
Co2MI	44.97 ±0.96	46.53 ±0.59	51.60 ±0.34	38.98 ±0.41	41.44 ±0.32	46.12 ±0.41	43.28 ±0.59
Cu4MI	42.57 ±1.40	44.92 ±0.81	52.71 ±0.72	30.84 ±0.90	31.77 ±0.32	38.35 ±0.47	46.66 ±0.35
Ni4MI	44.97 ±0.96	41.28 ±0.48	55.96 ±0.49	28.32 ±0.57	38.82 ±0.36	39.02 ±0.34	39.78 ±0.44
Co4MI	45.03 ±0.62	46.06 ±0.46	51.14 ±1.60	36.90 ±0.46	43.99 ±0.30	79.83 ±0.40	155.00 ±0.34

Table 4. The Shear Strength [MPa] of Aluminum Joints Obtained from Epoxy Adhesives after the Selected Days of Storage

Acronym of curing agent	Time of storage [days]		
	0	34	90
2MI	12.90±1.47	–	–
Cu2MI	14.50±5.33	15.50±1.68	11.88±2.15
Ni2MI	12.53±1.88	11.57±1.22	12.07±0.60
Co2MI	11.54±1.99	11.66±1.66	11.19±1.19
Cu4MI	10.42±1.04	8.67±2.87	12.83±1.14
Ni4MI	11.80±1.83	13.37±1.88	13.24±1.63
Co4MI	13.64±2.11	13.98±5.04	11.95±0.95

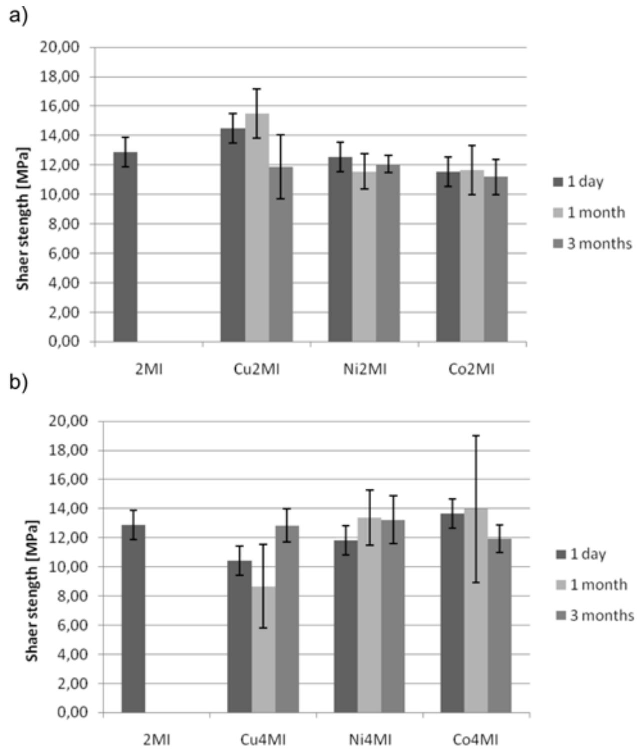

Figure 2. The shear strength of aluminum joints obtained from epoxy adhesives after the selected time of storage a) for epoxy adhesives hardened with imidazole complex in ratio 2:1; b) for epoxy adhesives hardened with imidazole complex in ratio 4:1

obtained directly after mixing the composition and after 1 and 3 months of storage.

Table 5. The Shear Strength [MPa] (by 120°C) of Aluminum Joints Obtained from Epoxy Adhesives after the Selected Days of Storage

Acronym of curing agent	Time of storage [days]		
	0	34	90
2MI	1.90±0.34	–	–
Cu2MI	9.53±0.89	6.26±1.18	5.84±1.27
Ni2MI	9.50±0.40	10.21±1.92	8.67±1.04
Co2MI	7.97±2.25	8.71±0.88	6.07±2.11
Cu4MI	9.25±1.44	8.23±1.95	10.12±0.78
Ni4MI	8.75±0.78	8.58±1.54	5.03±2.36
Co4MI	11.62±1.80	11.07±1.34	5.56±1.06

The shear strength measured at 120°C of aluminum joints obtained from epoxy adhesives hardened with imidazole complexes is much higher than the shear strength obtained using the reference formulation in spite of comparable glass transitions (table 3).

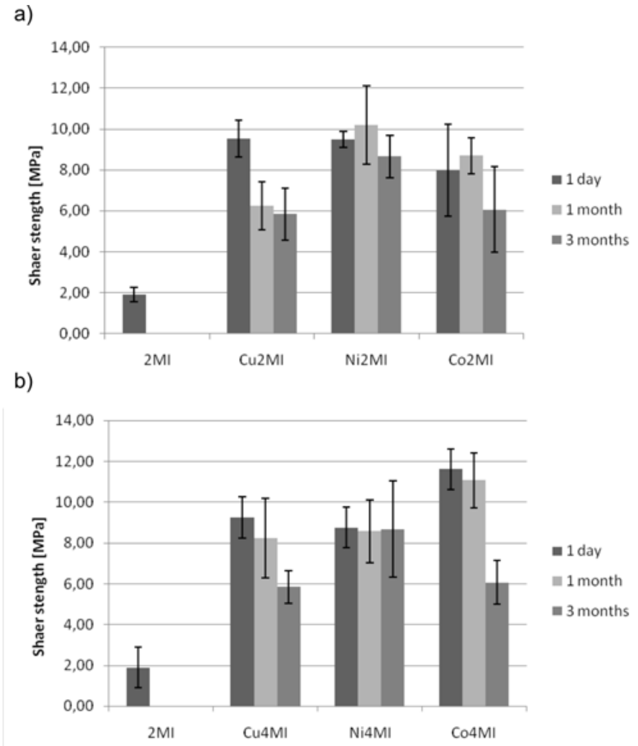

Figure 3. The shear strength of aluminum joints obtained from epoxy adhesives after selected time of storage a) for epoxy adhesives hardened with imidazole complex in ratio 2:1; b) for epoxy adhesives hardened with imidazole complex in ratio 4:1

In the case of shear strengths for aluminum joints obtained from epoxy resin and imidazole complexes, after 3 months of storage there can be observed a small decrease (for epoxy adhesives: Ni2MI and Cu4MI) of this parameter in comparison with the values obtained after mixing the adhesive compositions. The higher decreasing of this property after 3 months of storage is observed for the aluminum joint obtained with epoxy adhesives hardened Co4MI, Cu2MI complexes.

CONCLUSION

Complexes of 2-methylimidazole with metal cations: copper(II), nickel(II) and cobalt(II) can be used as latent curing agents for epoxy resins. The time of storage at room temperature can be longer than 3 months. The usage of these hardeners generally improves the shear strength in ambient temperature, especially in the case of using 2-methylimidazole complexes with nickel(II) cation. The shear strength is decreased with enlarging the time of storage epoxy compositions, the smallest influence of storage time can be observed for epoxy adhesives hardened with nickel(II) and imidazole complexes.

The obtained results are basis to further investigations of using imidazole and metal cation complexes as latent curing agent and properties of epoxy adhesives with usage of those hardeners.

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