

New Melamine–Formaldehyde–Ketone Resins. VI. Preparation of Filled Molding Compositions and Compression-Molding Materials from Reactive Solvents Based on Cyclohexanone

Dorota Głowacz-Czerwonka, Mieczysław Kucharski

Department of Organic Chemistry, Faculty of Chemistry, Rzeszów University of Technology, Aleja Powstańców Warszawy 6, 35-359 Rzeszów, Poland

Received 30 December 2008; accepted 21 October 2009

DOI 10.1002/app.31636

Published online 28 January 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The conditions and a method of preparing new molding compositions and filled compression-molding materials from melamine–formaldehyde–cyclohexanone resins are described. The resins were obtained from melamine solutions in a reactive solvent prepared by the reaction of 1 mol of cyclohexanone with 7 mol of formaldehyde. The fillers were wood powder and sulfite cellulose. The thermal properties of the samples prepared from the compositions were studied with dynamic thermal anal-

ysis, thermogravimetry, and differential scanning calorimetry analysis. Selected mechanical properties [Brinell hardness, unnotched impact strength (Charpy method), and bending strength] of the cured resins were also measured. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2802–2807, 2010

Key words: fillers; mechanical properties; molding; resins; thermal properties

INTRODUCTION

Melamine-containing polymeric materials exhibit improved thermal stability and good dielectric properties because of the presence of *s*-triazine rings.¹ The use of melamine, however, as a monomer in products other than melamine–formaldehyde resins is limited by its poor solubility in water and most organic solvents.² A new group of so-called reactive solvents of melamine has been developed in the last decade. The reactive solvents, for example, solvents based on formaldehyde and cyclohexanone, not only dissolve melamine physically but also react with melamine, building into its structure.^{2–6} The resulting viscous resinlike solution can be used as a binder in melamine–formaldehyde–cyclohexanone (Mel–F–CH) molding compositions and filled compression-molding compounds.

This article is the sixth part of a series on new melamine–formaldehyde–ketone resins prepared with reactive solvents of melamine. It deals with preparation of molding compositions and the products that were prepared from them in the process of compression molding. In the following parts of the

series, compression-molding materials prepared from the melamine–formaldehyde–butanone system, as well as polyurethane foams prepared from the same resins, will be described.

EXPERIMENTAL

Chemicals

Pure cyclohexanone (Chempur, Piekary Śląskie, Poland), pure formalin (Standard, Lublin, Poland), sulfite cellulose bleached from coniferous trees (International Paper, Kwidzyna, Poland), wood powder (Chemical Plants ERG, Pustków, Poland), *pro analysis* melamine (Fluka, Buchs, Switzerland), and *pro analysis* triethylamine (Fluka) were used.

Synthesis of the reactive solvent and dissolution of melamine

The reactive solvent (code name 7-HMCH) was obtained in the reaction of cyclohexanone (1 mol) with formaldehyde (7 mol) according to the procedure described in a previous article.⁵ Then, the resulting reactive solvent was diluted with 20 wt % water (cf. refs. 5 and 6) and melamine in such an amount (45.5 g/100 g of reactive solvent) to obtain a liquid of sufficiently low viscosity at room temperature to mix with the cellulose filler.

Correspondence to: D. Głowacz-Czerwonka (dglowacz@prz.rzeszow.pl).

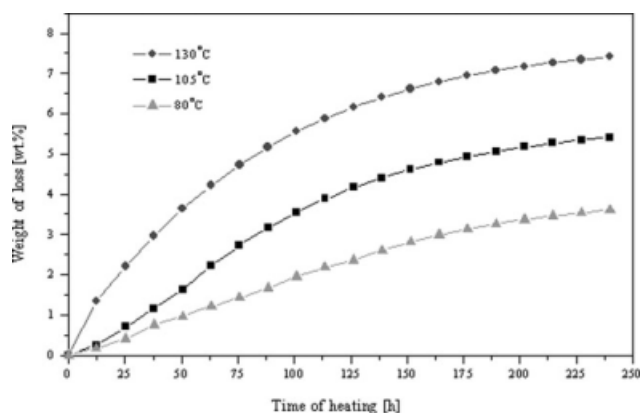


Figure 1 Weight losses of the Mel-F-CH compositions filled with wood powder (30 wt %) and dried at 80, 105, or 130°C.

all of medium or good fluidity, as expressed by the length of rods, which reached from 110 to 165 mm.

The Mel-F-CH compounds containing cellulose filler were white and fibrous and contained up to 7.0 wt % of water. Their molding index was in the range 125–165 mm, which classified the compositions among well-flowing ones (cf. Fig. 5).

The wood-powder-based compounds contained slightly more water (up to 8.1 wt %). Also, the molding index for these compounds was poorer than that for the cellulose-based ones, but still, the compounds could be classified as fairly well flowing.

As expected, as the content of filler increased, the molding index of the compounds decreased. This applied to both types of fillers. As the Mel-F-CH compounds were hygroscopic, their moisture content increased when they were left in air. The rate of this process depended on the air relative moisture and the thickness of the sample.

From the point of view of processing and product quality, the humidity of compounds should be kept as low as possible. More humid compounds require

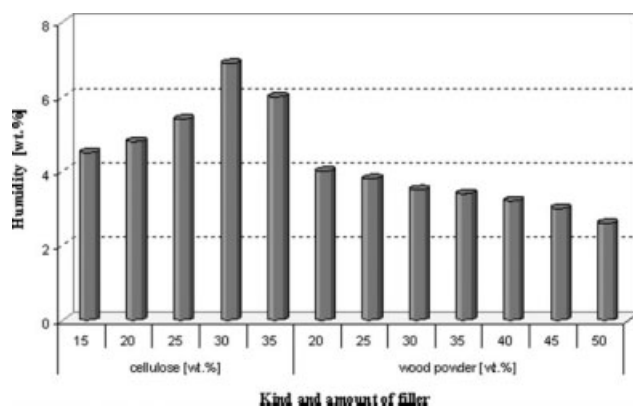


Figure 2 Humidity of the Mel-F-CH molding compositions expressed in terms of weight loss upon heating at 80°C to a constant weight.

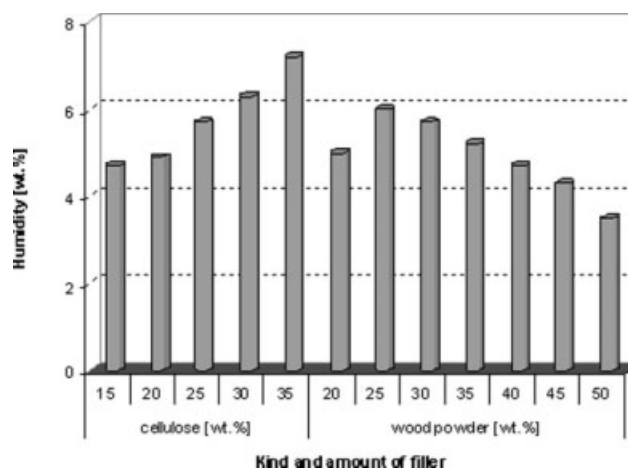


Figure 3 Humidity of the Mel-F-CH molding compositions expressed in terms of weight loss upon heating at 105°C to a constant weight.

longer pressing time and extensive degassing. Furthermore, the resulting samples had inferior appearance and worse thermal stability than the samples prepared from dry composition. The cellulose-filled samples were more hygroscopic than those filled with wood powder.

The thermal stability of the Mel-F-CH compounds was assessed by DTA and TG measurements in air and DSC analysis in a nitrogen atmosphere. The resulting thermograms are shown in Figure 6(A,B). As shown, several stages of the degradation process could be distinguished. Initial, a small weight decrease of the sample up to 110°C was due to the physical desorption of volatile organic substances and the evaporation of water. At about 120–150°C, a small endotherm appeared from the decomposition of unreacted O— and N-hydroxymethyl groups. This peak was absent in the analogous thermograms of the final molded pieces. A significant (10 wt %) weight loss was observed at 150–200°C.

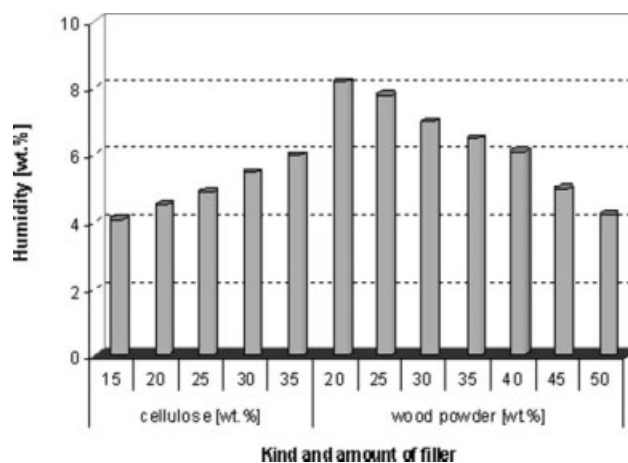


Figure 4 Humidity of the Mel-F-CH molding compositions expressed in terms of weight loss upon heating at 130°C to a constant weight.

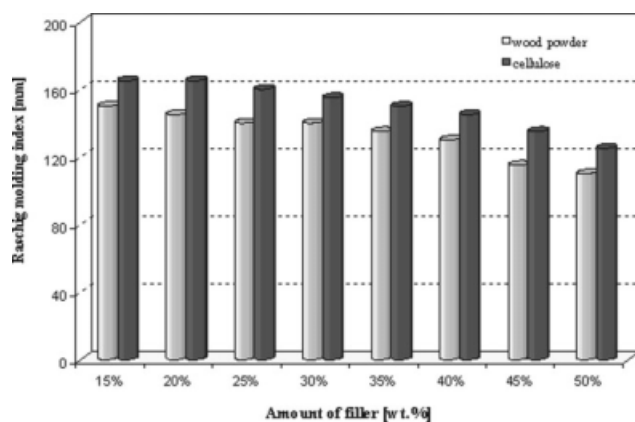


Figure 5 Effects of the kind and amount of the filler on Raschig's molding index (Raschig molding index of commercial Polomel MEC-3 = 120 mm) for the Mel-F-CH molding compositions.

weight loss was observed in the range 150–200°C (i.e., the cure temperature of the compounds). In the final molded pieces, this range of weight loss occurred at about 220°C (postcuring). Further heating brought about the start of decomposition of the samples. Above about 250°C, dimethyl ether groups converted into methylene groups with formaldehyde release. The surface area of the exothermic signals related to the cleavage of dimethyl ether and methylene bridges (in the range 260–310°C) was higher for the uncured compounds than for molded pieces. Above 310°C, the degradation process accelerated, with weight loss due to decomposition of cellulose glycoside rings (broad endothermic peak at about 320°C) and *s*-triazine rings (340–360°C). The broad exothermic signal on the DTA thermogram at 480–700°C, corresponding to the substantial weight loss seen on the TG curve, seemed to be due to the thermooxidation of the low-molecular-weight products of decomposition.

The DSC analysis (Fig. 7) seemed to confirm the conclusions from the DTA and TG measurements. Below 100°C, an endothermic peak appeared due to evaporating moisture. Then, another endotherm was seen at 120–140°C of a magnitude depending on the kind and amount of filler used. The peak seemed to be due to the melting of the small amount of *N*-hydroxymethyl derivatives of melamine present in the system. Finally, at 200–250°C, an endotherm due to the decomposition of dimethyl ether and methylene groups appeared; this was followed by the gradual decomposition of the whole sample with a distinct peak of melamine ring decomposition at about 340°C.

Mel-F-CH materials

The Mel-F-CH compounds prepared from melamine solutions in reactive solvents were compression-molded to form specimens for further study. The

obtained molded pieces (depending on the kind of filler) were white and fibrous (sulfite cellulose) or brown and powdery (wood powder).

The following mechanical properties were measured: bending strength, Brinell hardness, and unnotched impact strength (Charpy method). The results were compared with those for a cured commercial melamine-formaldehyde molding composition Polomel MEC-3 (Chemical Plants ERG, Pusków, Poland). The latter was a thermosetting material prepared by the impregnation of cellulose with melamine-formaldehyde resin and modified with some additives and dedicated to compression molding. The cellulose content was 30–35 wt %.

The hardness of the compression-molded Mel-F-CH specimens was found to increase with the content of filler. The highest value (136.7 MPa) was

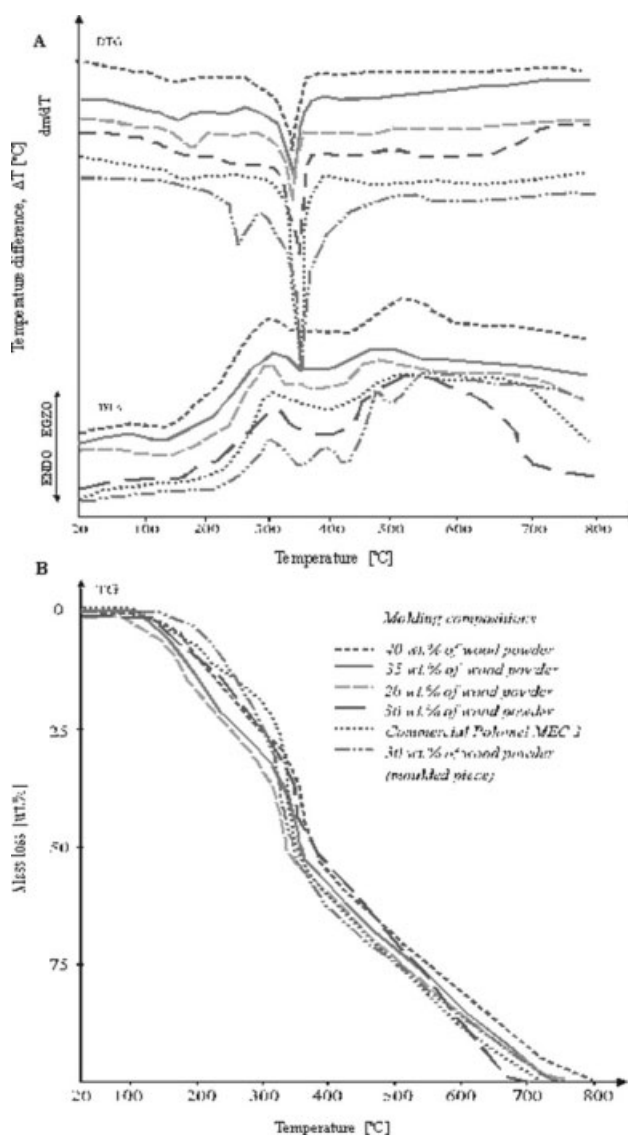


Figure 6 (A) DTA and (B) TG thermograms for the Mel-F-CH molding compositions containing different amounts of the wood powder filler.

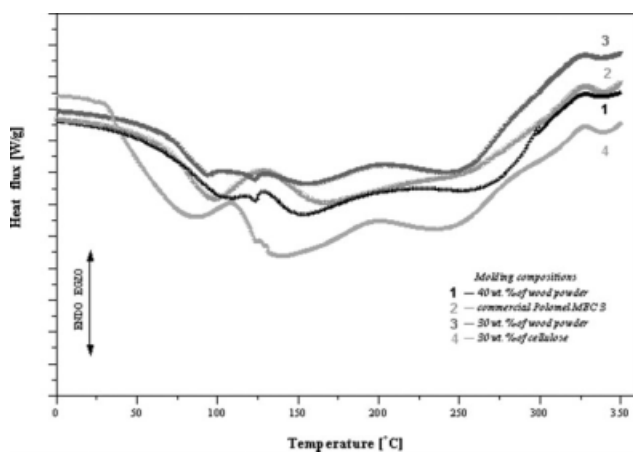


Figure 7 DSC thermograms of the Mel-F-CH molding compositions filled with cellulose or wood powder.

recorded for the sample containing 40 wt % sulfite cellulose. Then, it decreased with increasing cellulose content (Fig. 8). Generally, the cellulose filler provided better hardness in the samples. The molding compositions prepared in this study had much better hardnesses than the commercial product Polomel MEC-3. The latter had a Brinell hardness of only 84.4 MPa, as compared to 109.4 MPa recorded for the specimen prepared from the Mel-F-CH composition containing similar a cellulose content.

The impact strength of the cured Mel-F-CH compositions improved with increasing filler content (regardless of whether it was cellulose or wood powder) to reach the highest value of 3.8 kJ/m² for the sample containing 40 wt % cellulose. The impact strength of the wood-filled samples was somewhat smaller (cf. Fig. 9). Generally, the impact strength of the Mel-F-CH cured compositions was better than that of the Polomel MEC-3 samples (3.6 kJ/m²).

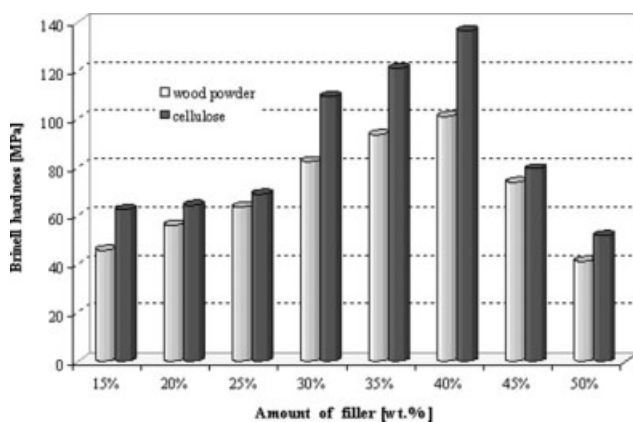


Figure 8 Effects of the kind and amount of the filler on the Brinell hardness (Brinell hardness of commercial Polomel MEC-3 = 84.4 MPa) for the Mel-F-CH molded samples.

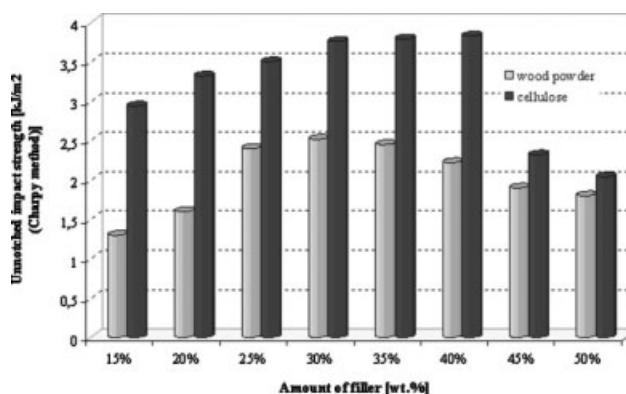


Figure 9 Effects of the kind and amount of the filler on the unnotched impact strength by the Charpy method (unnotched impact strength of commercial Polomel MEC-3 = 3.6 kJ/m²) for the Mel-F-CH molded samples.

The kind and amount of filler had different effects on the bending strength of the Mel-F-CH specimens (Fig. 10). As expected, the samples of cellulose-filled material had somewhat better strengths. When used in amounts up to 35 wt %, cellulose improved the strength. At higher contents, a decrease in the strength was observed. Similar behavior was observed for the samples filled with wood powder (the best filler content was 30 wt %). Again, the samples prepared from Mel-F-CH compositions had a better bending strength (72.1 MPa) than the samples prepared from the commercial composition Polomel MEC-3 (71.6 MPa).

The mechanical properties of the new Mel-F-CH molded materials depended on the type and amount of the filler. Cellulose used as a filler proved to provide somewhat better properties than the wood powder. This might have been caused by the higher content of hydroxyl groups in the former and, hence, stronger overall interactions with the functional groups of the resin (—OH, —NH— groups), mainly via hydrogen bonds.

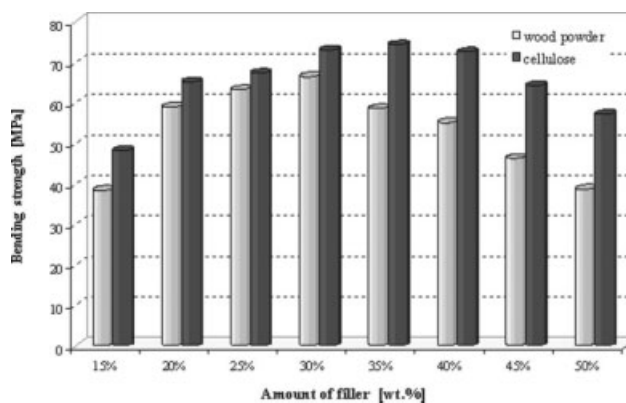


Figure 10 Influence of the kind and amount of the filler on the bending strength (bending strength of commercial Polomel MEC-3 = 71.6 MPa) for the Mel-F-CH molded pieces.

The effect of the filler content was also important. An amount exceeding about 45–50 wt % hampered the homogenization of the composition because of insufficient wetting of the filler by the Mel–F–CH resin.

In conclusion, the filled Mel–F–CH materials obtained with reactive solvents of melamine had good thermal and mechanical properties.

CONCLUSIONS

Mel–F–CH compositions are suitable materials for compression-molding processing that yields products of good thermal stability. Regardless of the kind of filler (cellulose or wood) used, the compositions had excellent molding indices when the amount did not exceed about 40 wt %.

The filled Mel–F–CH compositions obtained from melamine solutions in reactive solvents provided materials with better mechanical properties than those derived from the commercial melamine–formaldehyde product Polomel MEC-3. They had better hardness, impact, and bending strength values.

An improvement in the mechanical properties was observed as the amount of filler (either cellulose or wood powder) was increased to 30–40 wt %. A further increase in filler content did not lead to the property improvement.

Sulfite cellulose had the best properties as a filler. Its optimal content was about 35 wt %.

The filled compositions can be used as good-quality substituents of traditional melamine–formaldehyde resins.

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