Renewable Polyol-Based Polycarbamates and Polycarbamate–Formaldehyde Thermosetting Resins

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ABSTRACT: Several polycarbamates and polycarbamate–formaldehyde (CF) resins were synthesized, and their properties were investigated aiming at developing useful thermosetting polymer materials from simple polyols including those derived from renewable resources. Polycarbamates synthesized from polyols using two-step laboratory routes showed good storage stabilities making them suitable as large volume industrial chemicals. Furthermore, syntheses and ^{13}C-NMR studies of CF resins showed the formation of oligomeric resins having hydroxymethyl and methylene groups with thermosetting curing properties that are similar to those of current urea–formaldehyde (UF) resins. Dynamic mechanical analysis studies showed somewhat slower curing rates for CF resins compared to UF resins. Bonding of particleboard and internal bond and free formaldehyde content measurements indicated high-bond strength values and very low-formaldehyde emission potentials for CF resins. The higher functionalities of CF resins appear to be the basis of good performances. Further investigations on scalable synthesis methods for polycarbamates and on the expansion of CF resins' bonding capabilities would need to be investigated in the future. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2209–2220, 2011

Key words: renewable resources; renewable polyols; thermosets; polycarbamates; polycarbamate–formaldehyde resins; polycondensation

INTRODUCTION

One thrust of current research in North America has been aiming at increasing the use of renewable biomass for production of industrial chemicals via polyols derivable from cellulose and hemicelluloses components as well as glycerol derivable from various fats in biodiesel manufacturing processes.[1,2] Various new industrial uses of these polyols need to be developed. Because polyols are very limited in chemical reactivity, conversion to corresponding fully substituted polycarbamates would be an option to use for enhancing the reactivity. Conversion of monoalcohols to corresponding monocarbamates (R—OCO—NH$_2$) has been done by reacting with urea or sodium cyanate at elevated temperatures.[3–5] However, diols and polyols currently need to go through multistep procedures, such as reacting with phosgene[6–10] or its intermediate phenyl chloroformate[11] followed by a treatment with ammonia. Small-scale preparations could also be done by using acyl isocynates.[12,13]

On the other hand, the phosgene method would be the only method currently available for large-scale manufacturing of polycarbamates, but the barrier to its implementation is very high because of the toxicity of phosgene. Various other reaction methods of using sodium cyanate, urea, or simple alkyl carbamates were reported to be useful for the synthesis of polycarbamates of various 1,2-diols, but the yields are low and variable,[14–17] and probably polyols would encounter similar difficulties. Also, various approaches of using carbon dioxide with ammonia or amines have been investigated for carbamate group syntheses aiming at developing the desirable nonphosgene methods,[17–22] but these less toxic approaches have not been realized yet.

Among the various potential uses of polycarbamates, a few polycarbamate–formaldehyde (CF) resin polymers and applications were reported to be useful in patent literatures,[9,23,24] a development based on the similarity of carbamate groups to carbamide groups of urea and urea–formaldehyde (UF) resins. UF resins are currently used in large volumes as binders for interior-grade composite wood products and in other applications.[25] Specifically, diethylene glycol dicarbamate–formaldehyde resins were examined in coatings and yarn treatments,[23] and glycerol tricarbamate–formaldehyde (GCF) resins[9] and similar higher functionality CF resins[24] were examined for yarn treatments. However, these CF

resins are currently not well known or available in the industry for reasons obscure except the toxicity of phosgene to be needed in the manufacturing of polycarbamates. On the other hand, although the roadblock of phosgene toxicity exists, the chemical properties and potential utilities of polycarbamates and CF resins are needed to be explored further.

UF resins are currently used as binders of interior-grade wood composite boards such as particleboard, medium density fiberboard, and hardwood plywood, but these boards are beset with the well-publicized formaldehyde emission problem. Federal and state formaldehyde emission laws have been drastically tightened in recent revisions.[26,27] The formaldehyde emission problem of UF resin-bonded boards arises from the minor but significant reversion reactions in the UF resin chemistry,[28–30] that is, a small proportion of N-hydroxymethyl groups in UF resins reverses to formaldehyde gas in the thermosetting curing process. Although the reverse reaction is very minor in comparison with the forward, curing reaction process, its suppression would be possible only by increasing the amide group content in the resin system, that is, by adding more urea into the resin, resulting in lowering the crosslinking density and the strength of board. For CF resins made from polycarbamates having three or more carbamate groups, the reverse reaction of hydroxymethyl groups would be suppressed due to the higher functionality than in UF resins, which may be used either for lessening of formaldehyde emission or propping up the board strength. In this study, therefore, glycerol, meso-erythritol, D-xylitol, D-glucitol, D-mannitol, pentaerythritol, 1,1,1-trihydroxymethyl ethane, and 1,1,1-tris(hydroxymethyl)-propane, and ethylene glycol as a comparison were selected. These polyols were first fully derivatized to polycarbamates, and, then, CF resins were made by reacting with formaldehyde and characterized for chemical structures and thermosetting characteristics, and, further, selected CF resins were evaluated for their bonding and formaldehyde emission potentials as particleboard binders.
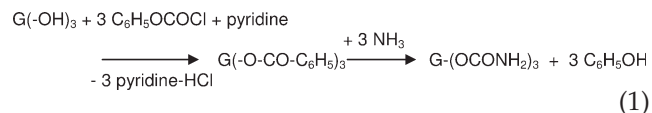
EXPERIMENTAL

Materials and methods

Phenyl chloroformate, trichloroacetyl isocyanate, tetrahydrofuran (THF), pyridine, methanol, urea, and polyols were purchased from Aldrich Chemical Co. Ammonia gas was purchased from Air Gas Co. A UF resin (control) was prepared at a mole ratio of 1.15.[31] Formaldehyde solution (50% in water) was donated by Georgia-Pacific Corp. resin plant, Louisville, MS, and used over a period by keeping it at 60°C to prevent separation. Viscosity measurements of CF resin solutions were carried out using the Gardner–Holdt

(GH) system at 25°C. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. Infrared (IR) spectra were obtained on Varian 3100 FTIR spectrometer on KBr pellet. ^{13}C-NMR spectra of polycarbamates were obtained in DMSO-d_6, and those of CF resins were obtained in water solutions as prepared with a small amount of DMSO-d_6 added as an internal reference and by Spectral Data Analysis, Champaign, IL. Quantitative conditions of 12-μs pulse-with, 15 s pulse-delay, and 400 scans were used and the peaks integrated. DMSO was dissolved well in CF resins and reduced the viscosity. In ^{13}C-NMR spectra of synthesized polycarbamates, the relative integration values of carbons corresponded closely to their molecular values, and therefore values greater than one are reported as integers in parenthesis.

Synthesis of glycerol tricarbamate using phenyl chloroformate and ammonia

This procedure was adapted from a similar reported procedure used for monoalcohols[11]:

$$G(-OH)_3 + 3\ C_6H_5OCOCl + pyridine$$
$$\xrightarrow[- 3\ pyridine\text{-}HCl]{} G(-O\text{-}CO\text{-}C_6H_5)_3 \xrightarrow{+\ 3\ NH_3} G\text{-}(OCONH_2)_3 + 3\ C_6H_5OH \quad (1)$$

In a 500-mL three-necked flask equipped with a stirrer, condenser, and thermometer, glycerol (14.8 g, 0.161 mol) was added and stirred in a mixture of pyridine (57.0 g, 0.73 mol) and THF (150 mL). Then, phenyl chloroformate (76.0 g, 0.484 mol) was added to the reaction mixture over an hour through a dropping funnel while keeping the reaction temperature below 60°C. The reaction mixture was stirred for 1 h and then cooled to room temperature, and the formed pyridine hydrochloride crystals were filtered off. The filtrate containing the "carbonate intermediate" was put in a three-necked flask equipped with a stirrer and thermometer, and ammonia gas was introduced over a period of 1 h to the saturation point. The reaction mixture was allowed to stir for two more hours, and then the solid precipitates of GC were collected by filtration. The crude product was purified by suspending in water followed by filtration and drying. Yield: 25.3 g (71.0%). mp 167–171°C.[9] ^{13}C-NMR [100 MHz, DMSO-d_6, Fig. 1(c), ppm]: 62.30 (2, CH$_2$), 156.28 (2, CO), 69.62, (CH), and 155.88 (CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1710, 1660, and 1560. Anal. Calculated for C$_6$H$_{11}$N$_3$O$_6$ (221.17): C, 32.58%; H, 5.01%, N, 19.00%. Found: C, 32.57%; H, 5.19%; N, 18.92%.

Synthesis of GC using trichloroacetyl isocyanate

This reagent has been used to derivatize simple alcohols to monocarbamates.[12,13]
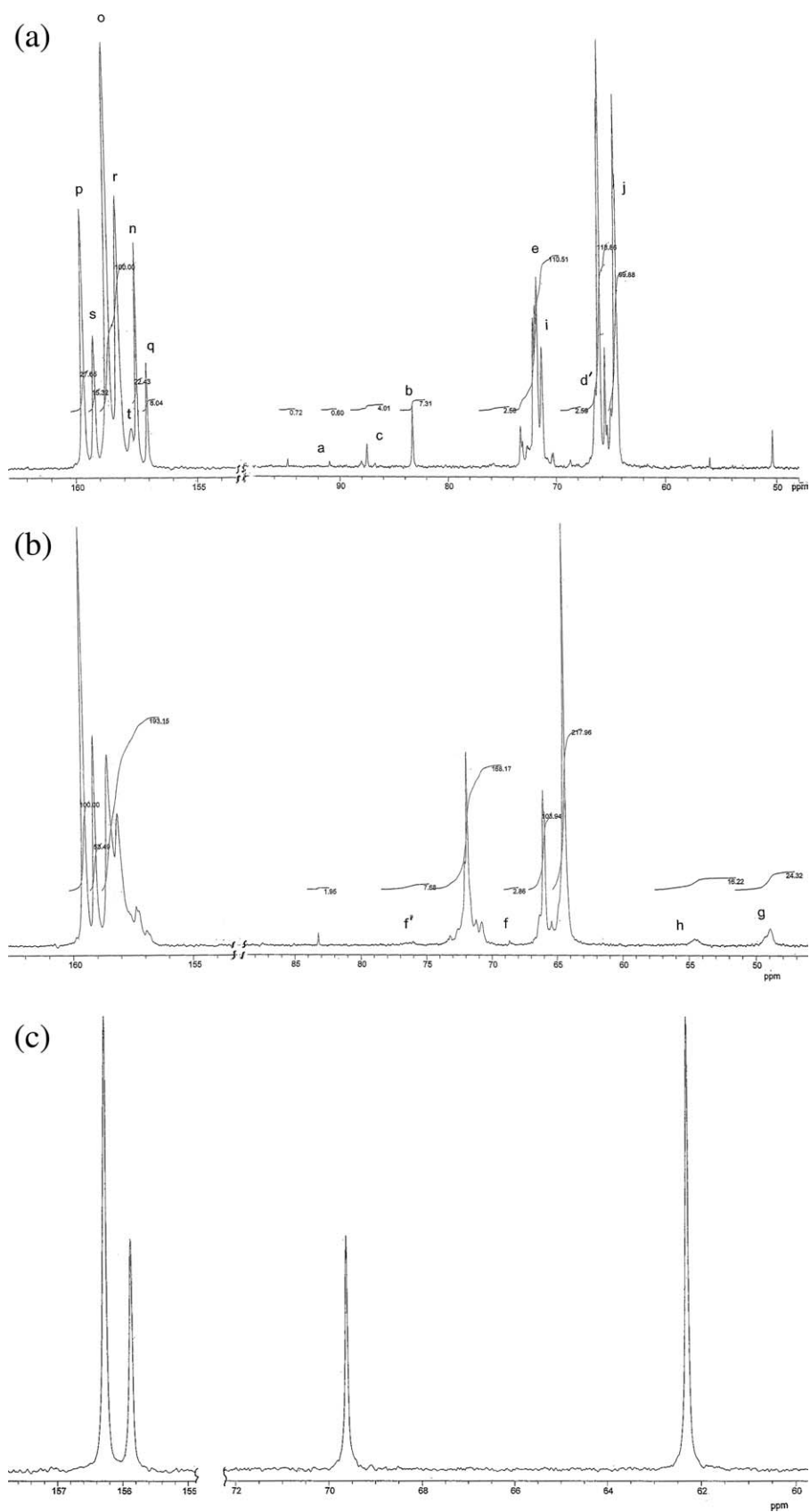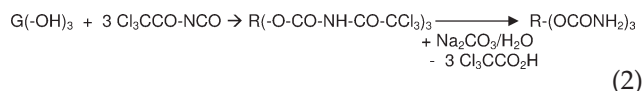
Figure 1 (a) ^{13}C-NMR spectrum of GCF1 resin with peaks identified with chemical structures shown in Figure 2. (b) ^{13}C-NMR spectrum of GCF2 resin with peaks identified with chemical structures shown in Figure 2. (c) ^{13}C-NMR spectrum of glycerol tricarbamate (GC) with chemical shift values indicated in the text.

$$G(-OH)_3 \; + \; 3 \; Cl_3CCO\text{-}NCO \rightarrow R(\text{-}O\text{-}CO\text{-}NH\text{-}CO\text{-}CCl_3)_3 \xrightarrow[-\;3\;Cl_3CCO_2H]{+\;Na_2CO_3/H_2O} R\text{-}(OCONH_2)_3$$

$$(2)$$

In a 100-mL three-necked flask equipped with a stirrer and thermometer, glycerol (1.48 g, 0.016 mol) was dissolved in acetone (40 mol), and the reactor was cooled in ice/water bath and then trichloroacetyl isocyanate (10.0 g, 0.053 mol) was added in drops over a period of 15 min while stirring. The reaction mixture was allowed to warm up to room temperature over a period of 30 min and stirred for 1 hour at room temperature. The reaction mixture was evaporated of acetone, and the residue taken in a mixture of methanol (40 mL) and water (10 mL) and sodium carbonate (0.50 g) was added and stirred at 50°C in a water bath. The precipitates of GC were collected by filtration and purified by recrystallization from hot water. Yield 2.71 g (75.9%) with mp 169–171°C.[9]

Synthesis of mesoerythritol tetracarbamate

The phenyl chloroformate method was followed using mesoerythritol (20.0 g, 0.160 mol), phenyl chloroformate (102.5 g, 0.656 mol), pyridine (76.0 g, 0.962 mol), and THF (250 mL). Yield: 24.5 g (52.1%). mp 275–276°C. ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 62.03(2, CH$_2$), 156.47(2, CO), 70.39(2, CH), and 155.89(2, CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1710, 1675, 1645, and 1610. Anal. Calculated for C$_8$H$_{14}$N$_4$O$_8$ (294.22): C, 32.66%, H, 4.80%, N, 19.04%. Found: C, 32.69%; H, 4.82%; N, 18.95%.

Synthesis of D-xylitol pentacarbamate

The phenyl chloroformate method was followed using D-xylitol (60.8 g, 0.40 mol), phenyl chloroformate (314.0 g, 2.0 mol), pyridine (176.0 g, 2.23 mol), and THF (1.0 L). Yield: 65.0 g (41.0%). mp 257–259°C. ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 62.77(2, CH$_2$), 156.43(2, CO), 69.71(3, CH), and 156.04(3, CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1710, 1675, 1645, and 1610. Anal. Calculated for C$_{10}$H$_{17}$N$_5$O$_{10}$ (396.27): C, 32.70%; H, 4.67%; N, 19.07%. Found: C, 32.75%; H, 4.80%; N, 18.56%.

Synthesis of D-glucitol hexacarbamate

The phenyl chloroformate method was followed by using glucitol (30.0 g, 0.165 mol), phenyl chloroformate (164.0 g, 1.04 mol), pyridine (84.0 g, 1.06 mol), and THF (500 mL). Yield: 54.0 g (74.4%). mp 277–280°C. ^{13}C-NMR (100 MHz, DMSO-d_6), ppm): 62.59 (CH$_2$), 156.43 (CO), 69.52 (CH), 155.79 (CO), 69.88(2, CH), 155.66(2, CO), 69.88 (CH), 155.59 (CO), 61.92 (CH$_2$), and 156.35 (CO). IR (KBr, cm^{-1}): 3420, 3415,

2985, 1710, 1675, 1640, and 1610. Anal. Calculated for C$_{12}$H$_{20}$N$_6$O$_{12}$ (440.32): C, 32.73%; H, 4.58%; N, 19.09%. Found: C, 32.56%; H, 4.76%; N, 18.40%.

Synthesis of D-mannitol hexacarbamate

The phenyl chloroformate method was followed using D-mannitol (19.0 g, 0.121 mol), phenyl chloroformate (101 g, 0.643 mol), pyridine (80 g, 1.01 mol), and THF (250 mL). Yield: 32.5 g (61.0%). mp 290–305°C. ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 61.97(2, CH$_2$), 156.47(2, CO), 70.24(2, CH), 155.82(2, CO), 70.13(2, CH), and 155.61(2, CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1710, 1670, 1640, and 1610. Anal. Calculated for C$_{12}$H$_{20}$N$_6$O$_{12}$ (440.32): C, 32.73%; H, 4.58%; N, 19.09%. Found: C, 32.83%; H, 4.89%; N, 17.71%.

Synthesis of pentaerythritol tetracarbamate

The phenyl chloroformate method was followed using pentaerythritol (21.37 g, 0.157 mol), phenyl chloroformate (100.0 g, 0.637 mol), pyridine (80.0 g, 1.05 mol), and THF (250 mL). Yield: 33.5 g (69.30%). mp 270–274°C.[9] ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 42.24 (C), 62.09(4, CH$_2$), and 156.48(4, CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1710, 1675, and 1600. Anal. Calculated for C$_9$H$_{16}$N$_4$O$_8$ (308.25): C, 35.01%; H, 5.23%; N, 18.18%. Found: C, 34.92%; H, 5.35%; N, 17.88%

Synthesis of 1,1,1-tris(hydroxymethyl)-ethane tricarbamate

The phenyl chloroformate method was followed using 1,1,1-tris(hydroxymethyl)-ethane (25.23 g, 0.21 mol), phenyl chloroformate (100.0 g, 0.637 mol), pyridine (80.0 g, 1.05 mol), and THF (250 mol). Yield: 36.7 g (70.2%). mp 175–179°C. ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 16.45 (CH$_3$), 38.72 (C), 65.21(3, CH$_2$), and 156.71(3, CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1715, 1690, and 1610. Anal. Calculated for C$_8$H$_{15}$N$_3$O$_6$ (249.22): C, 38.55%; H, 6.07%; N, 16.86%. Found: C, 38.54%; H, 6.14%; N, 16.88%.

Synthesis of 1,1,1-tris(hydroxymethyl)-propane tricarbamate

The phenyl chloroformate method was followed using 1,1,1-tris(hydroxymethyl)-propane (84.0 g, 0.626 mol), phenyl chloroformate (307.0 g, 1.95 mol), pyridine (240.0 g, 3.16 mol), and THF (750 mL). Yield: 121.0 g (73.5%). mp 162–164°C. ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): 7.47 (CH$_3$), 22.50 (CH$_2$), 40.08 (C), 63.40(3, CH$_2$), and 156.71(3, CO). IR (KBr, cm^{-1}): 3420, 3415, 2985, 1710, 1685, and 1595. Anal.

Calculated for $C_9H_{17}N_3O_6$ (263.25): C, 41%.06; H, 6.51%; N, 15.96%. Found: C, 41.07%; H, 6.58%; N, 15.98%.

Synthesis of ethylene glycol dicarbamate

The phenyl chloroformate method was followed using ethylene glycol (62.0 g, 1.00 mol), phenyl chloroformate (330 g, 2.10 mol), pyridine (165.0 g, 2.10 mol), and THF (700 mL). Yield: 120.0 g (81.1%). mp 169–170°C, agreed with reported value.[17]

Synthesis of glycerol tricarbamate–formaldehyde resins

Formaldehyde (F) (33.0 g, 50.0% solution, 0.55 mol) and water (32.0 g) were charged into a 250-mL reaction flask equipped with a cooling condenser, thermometer, stirrer, and heating mantle, and the solution pH adjusted to 8.5 using 8% sodium hydroxide. The formaldehyde solution was heated to 80–90°C, and glycerol tricarbamate (44.0 g, 0.18 mol) was added (F mol ratio 3.06) over a period of 20 min, and heating was continued to maintain the reaction mixture at 90°C for 10 min. Some exotherm was observed in this period. The reaction mixture became clear. The reaction was continued for 30 min at the same temperature and a sample taken (GCF1 resin) showed a viscosity of "A1-A" by GH scale and analyzed by ^{13}C-NMR spectroscopy, which indicated that the hydroxymethylation reaction was completed at this stage.

The resin mixture was reacted further to make oligomeric resins by adjusting the pH to 2.0 using 8% sulfuric acid and heating to 95°C. The viscosity of the reaction mixture increased to "H" in 4.5 h, when the reaction was ended by adjusting the pH to 8.0 using 0.8% sodium hydroxide and cooling to room temperature to give the finished resin sample (GCF2 resin). Drying of 1.0 g of resin at 125°C for 2.0 h gave a resin solid content of 61.0%.

Addition of urea to the GCF synthesized above (GCF2 + U)

Urea was found to dissolve well in all synthesized CF resins to give homogeneous mixes. As an example, urea (5.37 g, 0.09 mol) was added to GCF2 resin (100 g) synthesized above. The overall formaldehyde mol ratio was 2.0 and viscosity of resin was G by GH scale.

Mesoerythritol tetracarbamate–formaldehyde resin

The above procedure for GCF resin was followed: formaldehyde (8.40 g, 50% solution, 0.14 mol), water (15.0 g), and mesoerythritol tetracarbamate (10.0 g,

0.034 mol) were reacted at 80–90°C in the alkaline pH for 20 min (F mol ratio of 4.12) and then at pH 2.5 for 3.0 h. Because some separation of resin polymers occurred, some water was evaporated to yield 17.0 g of homogeneous condensation products having a resin-solids content of 82.0%.

Xylitol pentacarbamate–formaldehyde resin

The above procedure for GCF resin was followed with some variations: formaldehyde (30.0 g, 50% solution, 0.50 mol), water (33.3 g), and D-xylitol pentacarbamate (36.7 g, 0.10 mol) were reacted at pH 8.7 and 90–95°C (F mol ratio of 5.0). The reaction mixture became clear after 35 min and reacted further for 25 min. The reaction mixture was acidified to pH 1.5 and kept at 98°C. The viscosity of the reaction mixture increased from A_1A by GH scale to EF after 40 min, after which the reaction was ended by adjusting the pH to 8.0 and cooling. The resin solids content was found to be 51.0%.

D-Glucitol hexacarbamate–formaldehyde resin

The above procedure for GCF resin was followed with some variations of more water, and a longer alkaline reaction time: formaldehyde (8.20 g, 50% solution, 0.137 mol), water (15.0 g), and D-glucitol hexacarbamate (10.0 g, 0.023 mol) were reacted at pH 8.5 and 90°C for 3.0 h (F mol ratio of 5.96) to reach the clear solution stage. No acidic reaction was carried out. The viscosity value reached D by GH scale, and the resin solids content was found to be 36.2%.

D-Mannitol hexacarbamate–formaldehyde resin

The above procedure for GCF resin was followed with some variations of more water and a longer alkaline reaction time: formaldehyde (8.20 g, 50% solution, 0.137 mol), water (15.0 g), and D-mannitol hexacarbamate (10.0 g, 0.023 mol) were reacted at pH 8.5 for 3.0 h (F mol ratio of 5.96) to reach the clear solution stage (F mol ratio of 5.96). No acidic reaction was carried out. Viscosity was D by GH scale, and the resin solids content was found to be 35.5%.

1,1,1-Trihydroxymethyl ethane tricarbamate–formaldehyde resin

The above procedure for GCF resin was followed with minor variations: formaldehyde (28.0 g, 50% solution, 0.47 mol), water (32.0 g), and 1,1,1-trihydroxymethyl ethane tricarbamate (40.0 g, 0.16 mol) were reacted (F mol ratio of 3.0) at pH 8.5 and 85°C for 40 min. Resin sample TECF1 was taken. Then, the reaction mixture was further reacted at pH 1.77 and

95°C for 1 h until a viscosity of B reached when the reaction was ended by cooling and pH adjustment to 7.0 (Resin sample TECF2). The resin solids content was found to be 54.0%.

1,1,1-Trihydroxymethyl propane tricarbamate–formaldehyde resin

The above procedure for GCF resin was followed with minor variations: formaldehyde (6.80 g, 50% solution, 0.11 mol) and 1,1,1-trihydroxymethyl propane tricarbamate (10.0 g, 0.038 mol) were reacted at pH 8.5 and 90°C (F mol ratio of 2.90) for 1.0 h. Approximately 5.0 g of water was evaporated, and the reaction mixture was cooled. No acidic reaction was carried out. Viscosity value was G by GH scale, and the resin solids content was found to be 76.0%.

Pentaerythritol tetracarbamate–formaldehyde resin

The above procedure for GCF resin was used with minor variations: formaldehyde (42.0 g, 50% solution, 0.70 mol), water (30.0 g), and pentaerythritol tetracarbamate (61.6 g, 0.20 mol) were reacted at pH 8.5 and 90°C (F mol ratio of 3.50) for 140 min, and a sample was taken (PTCF1 resin). Then, the reaction was continued at pH 2.8 and 95°C for 3.0 h to reach viscosity G by GH scale. The reaction was ended by adjusting the pH to 5.5 and cooling to room temperature to give PTCF2 resin. The resin solids content was found to be 60.0%.

Ethylene glycol dicarbamate–formaldehyde resin

The above procedure for GCF resin was followed with minor variations: formaldehyde (43.0 g, 50% solution, 0.72 mol), water (40.0 g), and ethylene glycol dicarbamate (60.0 g, 0.40 mol) were reacted at pH 8.5 and 93°C for 70 min (F mol ratio of 1.80) and cooled. No acidic reaction was carried out. Resin viscosity was E by GH scale, and the resin solids content was found to be 55.0%. The resin freezes on standing at room temperature and liquefies on heating.

UF resin as a control[31]

Formaldehyde (300.0 g, 50% solution, 5.0 mol) and urea (143 g, 2.38 mol) were reacted at pH 8.0 and 70–90°C for 30 min and further reacted at pH 5.0 and 95°C for about 110 min to advance to T viscosity by GH scale. The reaction mixture was adjusted to pH 8.0 and cooling applied to reach about 60°C, when urea (118 g, 1.97 mol) was added and stirred until the resin cooled to room temperature (F mol ratio of 1.15). About 8% sodium hydroxide and 8% sulfuric acid were used for all pH adjustments. The

resin viscosity of K by GH scale and solids content of 62.5% were obtained.

Curing analyses using a dynamic mechanical analyzer

DMA 983 from TA Instruments was used to evaluate thermosetting (curing) characteristics of synthesized CF resins.[32,33] In this test, a small given amount of resin is impregnated on to a fiberglass braid (1.25 mm w × 18.5 mm l × 0.15 mm t), which is then clamped between the two arms of instrument. When the test is started, the two arms periodically (1.0 Hz) stress the rectangular sample in the shear mode with an amplitude of 0.8 mm, and the sample chamber is heated at 25°C/min from room temperature to 160°C, 180°C, or 200°C, respectively, and then kept isothermal for 25 min. Figure 3 shows the DMA results of GCF2 resin, where the resin-impregnated braid started from zero shear modulus and reached, by curing, to the *maximum shear modulus*, which often stays at the same value or decreases in succeeding period depending on the *heat stability* of cured resin. From this graph, the *cure time* (*min*) is also obtained as the time to reach the maximum shear modulus point. In the measurement of shear moduli, the thickness of cured fiberglass braid is manually measured and incorporated in the calculation of the curve to compensate for the small resin load weight differences often occurring in the sample preparation stage. Maximum shear modulus, cure time, and stability of cured resins were obtained for all synthesized resins. Modulus values obtained are used only as relative values.

Bonding of wood particleboard with selected CF resins and control UF resin and testing for internal bond strengths and free formaldehyde contents. Small laboratory particleboards with dimensions of 6" × 6" × 0.5" and target board density of 50 pounds per cubic feet were made according to the common laboratory procedure.[34] Synthesized GCF2 and PTCF2 were adjusted to the formaldehyde mole ratio of 1.15 by adding calculated amounts of urea to match with that of control UF resin. Southern pine wood particles were used. The resin solids loading levels were 10.0% based on wood weight, and board mats were pressed for 4.0 min at 160°C for UF resin control and at 210°C for GCF2(+U) and PTCF2(+U) resins. CF resins were catalyzed to pH 1.9 using dilute sulfuric acid, and UF resin control was catalyzed with ammonium sulfate at 0.5% level based on liquid resin weight.[31] Four replicate boards were made, and average values were obtained. Internal bond strength tests were done according to the ASTM D1043 procedure. Free formaldehyde contents of boards were measured according to the European Standard (DIN EN 120-92) procedure. The
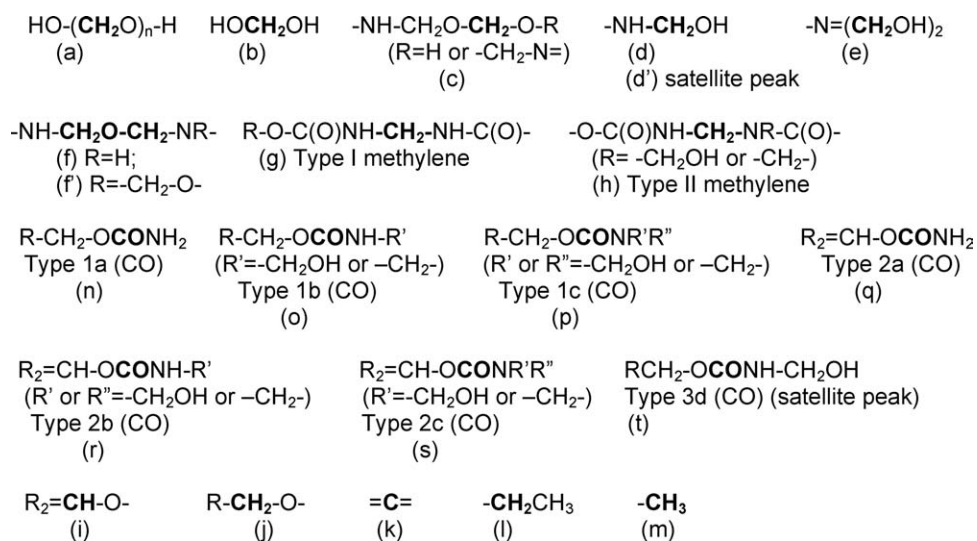
HO-(**CH₂O**)ₙ-H   HO**CH₂**OH   -NH-CH₂O-**CH₂**-O-R   -NH-**CH₂**OH   -N=(**CH₂**OH)₂
(a)   (b)   (R=H or -CH₂-N=)   (d)   (e)
                              (c)   (d') satellite peak

-NH-**CH₂O-CH₂**-NR-   R-O-C(O)NH-**CH₂**-NH-C(O)-   -O-C(O)NH-**CH₂**-NR-C(O)-
(f) R=H;   (g) Type I methylene   (R= -CH₂OH or -CH₂-)
(f') R=-CH₂O-   (h) Type II methylene

R-CH₂-O**CO**NH₂   R-CH₂-O**CO**NH-R'   R-CH₂-O**CO**NR'R"   R₂=CH-O**CO**NH₂
Type 1a (CO)   (R'=-CH₂OH or –CH₂-)   (R' or R"=-CH₂OH or –CH₂-)   Type 2a (CO)
(n)   Type 1b (CO)   Type 1c (CO)   (q)
                 (o)   (p)

R₂=CH-O**CO**NH-R'   R₂=CH-O**CO**NR'R"   RCH₂-O**CO**NH-CH₂OH
(R' or R"=-CH₂OH or –CH₂-)   (R'=-CH₂OH or –CH₂-)   Type 3d (CO) (satellite peak)
Type 2b (CO)   Type 2c (CO)   (t)
(r)   (s)

R₂=**CH**-O-   R-**CH₂**-O-   =**C**=   -**CH₂**CH₃   -**CH₃**
(i)   (j)   (k)   (l)   (m)

Figure 2 Chemical structures of CF resins identified with letters (a) ∼ (t).

procedure, briefly, involves the extraction of formaldehyde from cut particleboard (100.0 g) by refluxing it in toluene (600 mL) for 2 h. The toluene vapor containing formaldehyde is captured in the condenser, and, continuously, the condensates are percolated through a water layer (1.0 L) for transfer of formaldehyde into the water layer. The water layer is then tested for formaldehyde content by the colorimetric method (Spectronic 20 of Bausch and Lomb at 412 nm) after reacting with 2,4-pentanedione in ammonium acetate buffer solution.

RESULTS AND DISCUSSION

Syntheses and characterization of polycarbamates

The chemical structures of synthesized polycarbamates were agreed well with ^{13}C-NMR, melting point, IR spectroscopy, and elemental analysis results. All synthesized polycarbamates were nonhygroscopic and stable indefinitely at room temperature as well as in heating for melting point determinations or in brief treatments in water. ^{13}C-NMR chemical shift values compared well with those of starting polyols or their acetates. Also, the spectral integration values of different carbons in a molecule agreed with the expected molecular structures. For example, glycerol backbone carbons of glycerol triacetate occur at 62.2 and 69.2 ppm, respectively (Aldrich spectrum T4, 370-2), and the carbamate group of butyl carbamate occurs at 157.5 ppm (Aldrich spectrum B9, 080-7), which compare well with 62.30, 69.62, and 155.88 and 156.28 ppm of GC. The carbamate carbonyl groups of all synthesized polycarbamates occurred in the narrow range of 155.61–156.70 ppm. Melting points of synthesized GC and PTC agreed with reported values,[9] where the synthesis procedures were similar using phenyl

chloroformate but different reaction solvents. All synthesized polycarbamates gave sharp melting points. The storage, heat, and water stabilities of synthesized polycarbamates were judged to be good for use as raw materials for common large volume thermosetting resins. This observation agrees with some reported observations that ethyl carbamate molecular structures are stable to mild acid, base, or anhydrous ammonia treatments.[5]

Synthesis and ^{13}C-NMR characterization of CF resins

Organic carbamate groups have been known to react with formaldehyde similarly to the carbamide groups of UF resins. For example, ethyl carbamate reacts with formaldehyde to form a cyclic trimer via forming three methylene bonds.[5] Patent literature reported diethylene glycol dicarbamate–formaldehyde-type and GCF-type resins,[9,23,24] but detailed structural determinations were not reported. In Figure 1(a–c), ^{13}C-NMR spectra of GCF1 and GCF2 resins and GC (as a comparison) are shown with chemical shift assignments of resins. The chemical structures in relation to ^{13}C-NMR chemical shift assignments are shown in Figure 2.

The chemical shifts of various carbons of CF resins were assigned by comparing with those of UF resins[31] and starting polycarbamates and by using ^{13}C-NMR substituent group effects,[35] and the results of all CF resins are summarized in Table I. Chemical shift values of CF resin backbone carbons moved slightly from those of corresponding polycarbamates due to one or two hydroxymethyl or methylene groups introduced on the amide groups with the magnitudes generally being in accord with the group substitution effects. Among formaldehyde-

TABLE I
^{13}C-NMR Chemical Shift Assignments of CF Resins in Water Solution with DMSO-d_6 (ppm)[a]

Groups	GCF[b]	ETCF	XTCF	GHCF	MHCF	TECF	TPCF	PTCF	EGCF	UF[a]
−NH−CH₂OH (d)	66.08(d)	66.46(d)	66.19(d)	66.08	66.3	66.06(d)	65.85(d')	66.21(d)	66.08(d)	65.2
(d')	66.34(d')	65.82(d')	66.52(d)			66.52(d')	66.37(d)	66.67(d')	66.56(d')	
−N= (CH₂OH)₂ (e)					~71–73	71.19	70.39	71.88	70.62	72.0
	~71–73	~71–73	~70–71	~70–71		71.60	70.69	71.34	70.27	
								70.34	70.08	
−NH−CH₂−NH− (g)	48.54		50.43			48.90		49.08	50.33	47.1
−NH−CH₂−NR− (h)	54.01					54.25		54.24		53.9
−NH−CH₂OCH₂−NH− (f)	68.66	69.10	69.38			70.1		70.41	69.08	69.5
−NH−CH₂OCH₂−NR− (f')				75.82	~75	76.04		76,26		75.1
−NHCH₂O−CH₂OH (c)	87.48	87.38	87.50	87.81	87.5	87.49	87.30	87.60	87.58	87.0
				86.74						
HO−CH₂O−H (b)	83.28	83.39	83.40	83.31	83.61	83.39	83.38	83.53	83.5	83.1
H−(CH₂)ₙ−OH (a)			90.96			90.94				
−CO− (n-s)	159.66(p)	158.24(p)	159.38(p)	~156	~156	159.91(p)	158.58(p)	159.75(p)	158.65(p)	158
	159.21(s)	157.89(s)	158.79(s)	159.5	159.8	158.83(o)	157.75(o)	158.68(o)	157.91(o)	−164
	158.61(o)	157.53(o)	158.36(o)			158.23(t)	157.04(t)	158.05(t)	157.28(t)	
	158.29(r)	156.95(r)	157.86(r)			157.51(n)	156.52(n)	157.39(n)	156.80(n)	
	157.69(t)	156.36(t)	157.47(t)							
	157.47(n)	156.10(n)	157.17(q)							
	157.04(q)	155.80(q)	156.68(n)							
−CH₂−OCO− (j)	64.45	63.78	64.35	~63–65	~63–65	68.72	64.95	65.52	64.04	
	64.56	63.54	65.16			67.69	65.28	64.48	64.31	
	65.27					67.52		64.32	64.63	
=CH−OCO− (i)	~71–73	~71–73	71.78	~70–73	~71–73					
			71.37							
=C= (k)						40.12	42.3	44.96		
							42.21	44.03		
−CH₂− (l)							23.69			
CH₃− (m)						17.47	8.54			

[a] Internal reference DMSO-d_6 at 49.50 ppm.
[b] Abbreviations for resin samples are shown in the text. Lower case letters of structures are related to those in Figure 2.

derived groups, monohydroxymethyl groups occurred at about 66 ppm, gemdihydroxymethyl groups at about 72 ppm, and methylene carbons at 48.9 ppm for groups in the linear polymer chain and 54.6 ppm groups in the branched polymer, all very close to corresponding groups in UF resins.[22] Methylene groups that would appear in the 59 ppm region for groups in the doubly branched polymer chain were mostly undetectable and similarly methylene–ether groups that would appear in the 69 and 76 ppm regions in UF resins were very weak, probably due to the formaldehyde mol ratios used in resin syntheses and higher functionality of polycarbamates. Small amounts of free formaldehyde were still remained as formals and monomeric or polymeric forms in the 83–92 ppm region.

The carbonyl groups in CF resins occurred in the 156–160 ppm region as shown in Figure 1(a,b), slightly down-field from those of polycarbamates [Fig. 1(c)], reflecting the β- and γ-substituent effects of introduced hydroxymethyl or methylene groups. The substituent effects of gemdihydroxymethyl groups were greater than monohydroxymethyl groups, and, further, the carbonyl groups bonded to backbone oxymethine groups occurred down-field from those bonded to oxymethylene groups. This separation of carbonyl groups often allowed the estimation of unreacted, singly reacted, and doubly reacted carbamate groups.

Several uncertain assignments remained. First, gemdi-hydroxymethyl groups appeared as two peaks (0.41 ppm apart) at ∼ 72 ppm and monohydroxymethyl groups appeared at ∼ 66 ppm with a down-field satellite peak (0.47 ppm part) with about 5–10% intensity of the main peak, as shown in Figure 1(a,b). Also, peaks of carbonyl groups that are bonded to oxy-methylene backbone carbons appear to give an up-field satellite peak (t). These split peaks occurred in all synthesized CF resins, and they appear to be traceable to a rotational restriction present around the C(O)−N bonds, similarly as for amide groups.[36] The highly concentrated, viscous regime of resin samples would have favored such an environment and may be verifiable by variable-temperature studies. The other minor problem for quantitative analysis was the overlap in the 70–72 ppm region of gemdi-hydroxylmethyl groups with oxymethine backbone polyol carbon groups. In this

TABLE II
^{13}C-NMR Spectral Integration Results of Carbon Groups of Various CF Resins[a]

Resin	CH$_2$O	–NH–CH$_2$O– **CH$_2$OH**	–N=(CH$_2$OH)$_2$	–NH–CH$_2$OH	=CH–O–[a] Estimate	–CH$_2$–O–[a]	–NH–CH$_2$–NR–	–NH–CH$_2$–NH–	CO type 1a	–CO– type 1b	–CO– type 1c	–CO– type 2a	–CO– type 2b	–CO– type 2c	–CO– type 3d
GCF1	13	3	110	103	58	116	0	0	15	58	28	8	42	15	7
GCF2	2	8	59	104	109	218	16	24	5	85	100	13	69	54	21
ETCF	39	122	113	601	488	488	85	0	21	324	111	21	386	40	21
XCF	51	36	331	584	597	399	34	17[b]	120	213	92	82	342	128	57
GHCF	222	108	839	444	886	443	0	0	–	–	–	–	–	–	–
MHCF	71	63	277	103	206	103	0	0	–	–	–	–	–	–	–
TECF1	21	4	204	368		603	3	10[b]	100	311	143				70
TECF2	44	73	386	335		900	80	84	196	519	126				152
TPCF	5	0	59	150		150	0	0	27	100	43				19
PTCF1	30	71	569	894		1976	42	8[b]	220	1000	472				196
PTCF2	26	87	630	820		1793	38	48	245	1000	429				230
EGCF	59	0	287	1691		2348	0	18[b]	100	1529	421				225

[a] The Integration values are only relative values within each resin group.
[b] These methylene groups appeared 2–3 ppm downfield from typical values and are therefore tentative assignments. Resin notations are as in the text.

case, oxy-methine carbon intensities can be inferred from the oxy-methylene or other carbon intensities in the same spectrum and subtracted to obtain the gemdi-hydroxymethyl group contents. Also, the carbonyl carbon peaks in GHCF and MHCF resins were rather complex, disallowing detailed analyses, and one reason may be traced to the difficulties of long reaction times encountered in the resin synthesis steps as described below.

CF resin oligomer structures from quantitative ^{13}C-NMR data

Quantitative integration data of ^{13}C-NMR spectra of CF resins are summarized in Table II, and calculated molar quantities are reported in Table III. First, the molar quantities of carbonyl groups were relatively well correlated to the molar quantities of oxymethylene or oxymethine backbone carbons, allowing the averages be used in subsequent calculations. The formaldehyde mol ratio values thus calculated were very close to the actual charge values of resins as shown in Table III, as expected from the quantitative ^{13}C-NMR method used. The calculated values in Table III show the various structural compositions and changes occurred in resin synthesis reactions. For example, GCF1 resin made with a formaldehyde mol ratio of 3.06 showed that 93.0% of the formaldehyde has reacted to give 45.0% mono- and 48% gemdi-hydroxymethyl groups. Further, in GCF2 resin, 11.4% type I and 4.8% type II methylene groups were formed at the expense of corresponding amounts of hydroxymethyl groups of GCF1 resin. The combined methylene groups represented 0.36 mol per mole of starting glycerol tricarbamate, which is equated to an average degree of polymerization of 1.56 for GCF2 resin. These functional group changes were also reflected in the carbonyl group values. Other CF resins gave the similar molar quantities, except GHCF and MHCF resins, which showed some deviations. As noted in synthesis procedures, the latter two resins required higher levels of water and longer reaction times in the alkaline reaction. Some side-reactions appeared to occur, resulting in some deviations in NMR analysis. Overall, however, ^{13}C-NMR quantitative results of CF resins clearly showed that the hydroxymethylation reaction in the first alkaline reaction step, and the methylene group forming reaction in the acidic pH are occurring smoothly according to eq. (3).
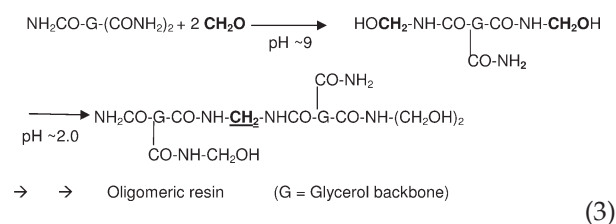
NH$_2$CO-G-(CONH$_2$)$_2$ + 2 **CH$_2$O** $\xrightarrow{\text{pH} \sim 9}$ HO**CH$_2$**-NH-CO-G-CO-NH-**CH$_2$O**H
                                                                    |
                                                                 CO-NH$_2$

$\xrightarrow{\text{pH} \sim 2.0}$ NH$_2$CO-G-CO-NH-**CH$_2$**-NHCO-G-CO-NH-(CH$_2$OH)$_2$
                                        |
                                    CO-NH-CH$_2$OH

→ →   Oligomeric resin   (G = Glycerol backbone)

(3)

TABLE III
Calculated Values of Chemical Structures of CF Resins from ^{13}C NMR Integration Results[a]

Resin	F mole ratio Charged	F mole ratio Measured	% Reacted F	% Charged F in Mono-HM (d)	Di-HM (e)	ME (g)	ME (h)	Amide (CO) (%) Free (n & q)	Mono-sub (o & r)	Di-sub (p & s)	CH$_2$ Content/mole and DP Mole	DP
GCF1	3.06	3.05	93.0	45.0	48.0			12.7	64.1	23.8	–	–
GCF2	3.06	3.17	94.9	50.2	28.5	11.4	4.8	5.2	54.2	44.4	0.36	1.56
ETCF	4.00	3.68	83.2	62.6	11.8	8.9	–	3.8	81.4	15.7	0.35	1.53
XCF	5.00	5.02	91.3	55.5	31.4	1.6	3.2	19.5	59.2	21.3	0.25	1.33
GHCF	5.96	7.26	79.5	27.5	52.0	–	–	–	–	–	–	–
MHCF	5.96	9.98	73.9	20.0	53.9	–	–	–	–	–	–	–
TECF1	3.00	2.92	95.8	61.6	34.2			16.1	61.0	23.0	–	–
TECF2	3.00	3.18	88.0	33.4	38.5	8.0	8.4	19.8	67.5	12.7	0.54	2.21
TPCF	2.90	2.66	97.7	70.4	27.3			14.3	63.0	22.7	–	–
PTCF1	3.50	3.76	90.4	54.0	36.4			11.7	63.4	25.0	–	–
PTCF2	3.50	3.60	93.1	50.0	38.4	2.9	2.3	12.9	64.6	22.5	0.19	1.22
EGCF	1.89	1.74	97.1	82.3	15.1			4.4	77.1	18.5	–	–

[a] Tentatively assigned methylene groups were not included calculations.

Abbreviations: F for formaldehyde; HM for hydroxymethyl groups; ME for methylene groups; DP for degree of polymerization; lower case alphabets relate to the chemical structure groups in Figure 3. Resin sample notations are described in the text.

Reaction rate differences in synthesis of CF resins compared to UF resins

In the first alkaline reaction step, polycarbamates dissolved in the formaldehyde solution at slower rates than in UF resins apparently due to their low solubility in water, and this tendency increased with increases of the molecular weights of polycarbamates. The reaction rates were still in the reasonable range up to XCF, but more water and significantly longer reaction times were needed for GHCF and MHCF resins, in which still some side reactions appeared to occur as discussed earlier. Furthermore, the second acidic reaction step also revealed significantly slower reaction rates for CF resins than UF resins: the acidic reaction of UF resins is normally completed within 2 h at pH 4.5–5.0 and 95°C, while CF resins were found to advance in viscosity only after the pH adjusted to 2.5 or lower under the similar temperature condition. Thus, the activation energy of the hydroxyl groups on the carbamate groups to form methylene carbocations (A) appears significantly higher than for carbamide group (B), shown in eq. (4).
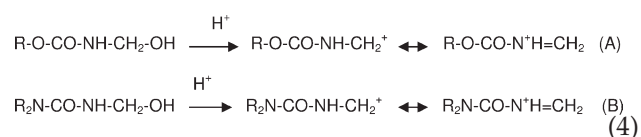
$$R\text{-}O\text{-}CO\text{-}NH\text{-}CH_2\text{-}OH \xrightarrow{H^+} R\text{-}O\text{-}CO\text{-}NH\text{-}CH_2^+ \leftrightarrow R\text{-}O\text{-}CO\text{-}N^+H{=}CH_2 \quad (A)$$

$$R_2N\text{-}CO\text{-}NH\text{-}CH_2\text{-}OH \xrightarrow{H^+} R_2N\text{-}CO\text{-}NH\text{-}CH_2^+ \leftrightarrow R_2N\text{-}CO\text{-}N^+H{=}CH_2 \quad (B)$$
$$(4)$$

TABLE IV
DMA Results of Various CF Resins and Control UF Resin Obtained at Three Curing Temperatures[a]

Resins	F moles/ amide group	160°C Max modulus (psi)	Cure time (min)	Stability	180°C Max modulus (psi)	Cure time (min)	Stability	200°C Max modulus (psi)	Cure time (min)	Stability
GCF2	3.06/3	4400	13.5	O	4300	9.5	O	700	7.5	O
GCF2(+U)	2.00/2.7	3550	11.5	O	–	–	–	–	–	–
ETCF	4.00/4	3350	11.0	O	3300	9.5	O	2750	7.5	O
XCF	5.00/5	3100	8.5	O	3100	7.4	O	3950	6.5	O
GHCF	5.96/6	–	–	–	4100	9.0	O	4600	6.5	M
MHCF	5.96/6	2850	9.5	O	–	–	–	–	–	–
TECF2	3.00/3	4300	11.5	O	5100	8.5	O	4400	7.5	M
TPCF	2.90/3	3700	14.0	O	3300	11.0	O	3300	5.5	O
PTCF2	3.50/4	4800	12.5	O	4250	9.5	O	4550	8.0	O
EGCF	1.89/2	1800	13.0	O	1750	8.0	O	2240	7.4	O
UF	1.15/2	1850	7.1	O	–	–	–	–	–	–

[a] GCF 2.75(+U): added urea to the F/(GC + urea) mole ratio of 2.0. F stands for formaldehyde; "O" indicates a good stability with no decrease and "M" indicates a small extent of degradation of max modulus in the 25-min standing period at final curing temperatures. Resin notations are described in the text.

This observation is significant in that uses of CF resins as adhesives, for example, would require higher acid catalyst strengths and therefore be restricted to substrates that are not that sensitive to acids. Wood substrates may be affected by this level of acids and need to be closely evaluated in future. On the other hand, the storage stability of CF resins when stored under neutral pH was far longer than UF resins, a positive attribute since UF resins in industry are stored and transported in neutral pH and catalyzed on site. Storage lives of UF resins are limited to 2–3 weeks at ordinary temperatures.

Thermosetting characteristics of CF resins from DMA

The DMA results are summarized in Table IV, and an example of curing diagram is shown in Figure 3. The results indicate that CF resins do undergo thermosetting (curing) reactions to reach the high modulus stages upon heating in 160–200°C ranges. Because CF resins in DMA runs were catalyzed only with 0.5% addition of ammonium sulfate similarly with the UF control resin, the observed curing times are directly comparable. At 160°C, common temperature used in the UF resin-bonded wood composite board industry, CF resins on average cured slower by 3–5 min than UF resin control, which is expected from the slower reaction rates observed in the acidic resin synthesis stage discussed earlier, and this implicates a significant decrease in plant productivity in comparison with UF resins. On the other hand, the curing times of CF resins at 200°C became shorter as expected and reached to the comparable values with that of UF resins at 160°C. CF resins thus might become comparably employable if the hot press temperature is to be increased to 200°C or higher. Here, one advantage of CF resins would be the good stability of cured resins even at 200°C while UF resins are not normally used at this high temperature because of poor stability of cured UF resins.
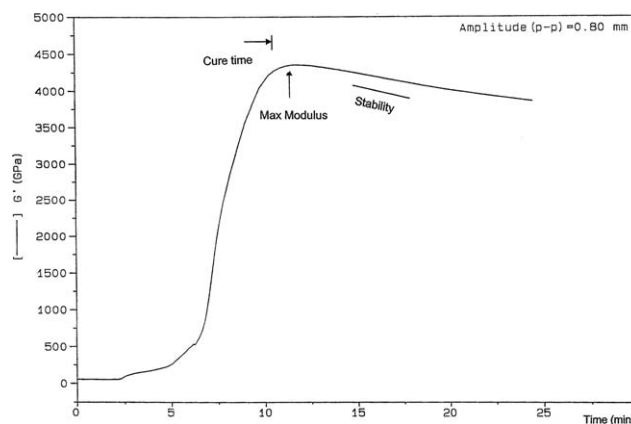

Figure 3 Dynamic mechanical analyzer curing results of GCF2 resin carried out at 180°C with measurement methods shown for the cure time, maximum shear modulus, and stability of cured resin.

The maximum shear modulus values of cured CF resins were significantly higher than UF resins at all temperatures, and even the values of CF resins obtained at 200°C are significantly higher than UF resins obtained at 160°C. These higher shear modulus values of CF resins relative to UF resins appear to be a strong positive expected of their higher functionalities. Although the functionality versus strength relationship in CF resins would require a more detailed work on the effects of formaldehyde mol ratios, the starting hypothesis advantage of higher functionality appears to be borne out.

Internal bond strengths and free formaldehyde contents of particleboard

GCF2(+U) and PTCF2(+U) resins, which were obtained by adjusting the formaldehyde mol ratio to 1.15, same as for control UF resin, showed significantly higher internal bond strength values, that is, 141–155 psi versus 110 psi. Furthermore, CF resins showed far better free formaldehyde content values, 4.0–4.1 mg versus 12.6 mg per 100 g of board. Although more detailed evaluation work is needed beyond this preliminary result, the low formaldehyde content values are also in line with the starting hypothesis of higher functionality effects of CF resins. The higher press temperature and/or stronger acid catalyst shown to be needed for CF resins may be ameliorated in future through detailed research to the ranges acceptable in the current particleboard industry.

TABLE V
Internal Bond Strength and Free Formaldehyde Contents of Particleboard[a]

	GCF2 (+U) resin	PTCF2 (+U) resin	UF resin control
Internal bond strength (psi)	141	155	110
Free formaldehyde content (mg/ 100 g wood)	4.1	4.0	12.6

[a] The formaldehyde mole ratios of all three resins used were equally 1.15. Resin notations are described in the text.

CONCLUSIONS

Various polyols including those derivable from renewable resources were derivatized to the corresponding polycarbamates using laboratory synthesis

routes. The polycarbamates were stable crystalline materials suited for large-scale industrial applications and were further shown to form CF oligomeric resins by reacting with formaldehyde under the alkaline and then acidic condition. CF resins were further shown to advance to highly rigid thermoset polymers and bond particleboard well when catalyzed with an acid to near pH 2.0 and heated up to 200°C, where resultant particleboard showed very low free formaldehyde contents compared with UF resins. CF resins were also shown to have ample storage stabilities under neutral pH condition compared to UF resins.

On the other hand, the acidity of catalyst needed for CF resins was substantially stronger, and the curing temperature also needs to be higher than current UF resins. Overall, however, the potential utility of CF resins was shown. Thus, simple polyols including those derivable from renewable resources were shown to have the polycarbamte route to lead to more reactive and therefore more useful materials such as in manufacturing of CF resins as an example. Glycerol and D-xylitol appear to be more suited for this purpose from renewability and processing feasibility in the derivatization and CF resin manufacturing processes. Thus, this study indicates that low cost, scalable manufacturing methods for polycarbamates including the phosgene method would be worthwhile to be developed in the future.

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