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A REVIEW

CURRENT TRENDS IN PREPARATION AND APPLICATIONS OF MELAMINE, MELAMINE FORMALDEHYDE, UREA–FORMALDEHYDE AND MELAMINE BASED POLYMERIC MATERIALS

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ABSTRACT

The current trends for synthesis of resins, polymers and blends of melamine–formaldehyde and urea–formaldehyde involving carbonisation, hydroxylation and etherification techniques have been presented. Several physico–chemical properties of them have been used for structure and molecular weight determination alongwith detailed description of thermal properties. The composites and various additives for desired properties of the products have been cited and the information is extracted from the literature between January 1997 to December 1999. The melamine resins and polymers have been elaborated in detail.

Key words : Melamine, Formaldehyde, Urea, Polymeric material.

Various features of melamine associated with its synthesis are highlighted to focus the utility and significance of the products of the melamine. Its solid from has been obtained directly from spray of melamine melt prepared from urea at high pressure. The melamine at melting point (MP) in a double jacketed vessel, with ammonia filled in jacket at 450°C and 1 to 4 mpa (milli Pascal) was reported to be converted to powder form. The conversion at temperatures between 200°C and its solidification point in presence of ammonia for 6 seconds to 5 hrs at 1 to 40 mpa was facilitated. The cooling of melamine melts[2] in an ammonia environment with ammonia pressure at < 200°C with mechanical agitation was found favourable. The pure solid melamine[3] from cooled melts in reactor by liquid ammonia from 50 to 350°C on transferring to an expansion vessel with ammonia for 1 minute to 5 hrs was obtained.

Spraying liquid melamine in a cooling vessel at 0.1 to 20 mpa and 50°C in presence of liquid ammonia made its dry powder[4]. Similarly multi crystal melamine[5] powders of 90 to 150 μm diameter (d), d50 < 50 μm with density 430 to 570 $kg.m^{-3}$, colour APHA < 17; melamine > 98.5% was made. The 99.5 to 99.5% melamine[6] has been manufactured from urea pyrolysis at liquid ammonia pressure and temperature. The 100 g melamine melt mixed with 100 g

ammonia at 80 mpa and 250°C for 45 minute at 3 mpa was reported to produce powder of 99.80 weight %. The melamine has been reported as a catalyst at high pressure and temperature that reduces operating pressure and temperature for converting hexagonal boron nitride particles[7] into cubic one. Where the cubic form has been useful for grinding, polishing, and cutting material in industries and melamine formaldehyde (MF) copolymer reported[8] to laminate resins preparation. By dissolving MF in formalin and successive condensation introduces storage stability, impregnation behaviour of resin and processing for lamination.

Reportedly, the Pd complex of MgO is seen to support preparation of melamine–formaldehyde polymer[9] and Pd catalytic behaviour for hydrogenation of nitroaromatics with carbonyl group was examined. It has been found that the nitro and carbonyl groups in p–nitrobenzaldehyde does sequentially hydrogenate to form p–aminobenzaldehyde and p–aminobenzyl alcohol (self condensation products), under similar conditions the nitro groups is also hydrogenated at o–nitrobenzaldehyde and p–nitroacetophenone. The nitro group is selectively hydrogenated at m–nitrobenzaldehyde product and with strong self condensation. The hydrogenation rates have been reported in order of p–nitroacetophenone > p–nitrobenzaldehyde > o–nitrobenzaldehyde > m–nitrobenzaldehyde. The low methylated melamine resin (I)[10] was produced with 85% solid formaldehyde and 37% liquid by hydroxymethylation and etherification. Solubility of low methylated (I) resin was increased from 1 : 1 to 1 : 20 (resin: water) ratio and mole ratios of solid formaldehyde (HCHO) to liquid HCHO and MeOH (methylated) to (I) in hydroxymethylation ratios were 3.5 : 1.5 and 1.4 : 6, respectively. Total dosage of MeOH was decreased from 30 to 25 moles in production with lower content of water in hydroxymethylation with solid HCHO instead of liquid HCHO as raw material. The methods like carbon anode materials were prepared by carbonisation of a formaldehyde–melamine resin[11] at 250°C for 4 hrs. It has been followed by pyrolysis, which undergoes at 400 to 900°C and carbonaceous material was then powdered and mixed with phosphoric acid heated at 100°C for 4 hrs.

The elements analysis, X–ray powder diffraction, BET and XPS (X–ray phosphorescence) techniques were used for estimation of effects of heat treatment and phosphorus doping on material. The temperature reported to affect nitrogen content, size of graphite crystallites and number of micropores at carbon anodes leading to reversible capacity changes and highest reversible capacity in materials was treated at 600°C. The phosphoric acid affects carbon structure and relative content of graphene nitrogen at high temperature, phosphorus doping results in enhancement of reversible capacity. An interaction of lithium is favoured along with reversible capacity making carbon suitable for use as anodes in lithium batteries. Woody pattern printed decorative paper[12] impregnated with melamine formaldehyde resin (I) at 120 g m^{-2}. A polyester non–woven fabric impregnated with (I) at 100 g m^{-2} and a parchment paper were successively laminated and hot pressed at 160°C and 15 kg cm^{-2} for 30°C. It gives 0.3 mm decorative sheet with good adhesion by ETOAC–rubber, and urea based adhesives with good

cracking resistance. The clay was encapsulated in various polymers as extender in paint and emulsions based on 2–ehyl–hexyl acrylate methyl–methacrylate copolymer binder[13], the porous encapsulants are MF resin, poly– (memethacrylate) and hexamethylene diaminehexamethylene diisocyanate polymers enhance hydrophobicity of clay particles, resulting in modification of freeze the stability, increased strength of paints and also to prevent agglomeration of water based paints.

The low order thermosetting resin[14] abrasives for sand blasting were manufactured for which 4 pieces of kraft paper were separately impregnated with 50% melamine–formaldehyde copolymer solution (viscosity 70 cp at 25°C). It has been noticed that a dried, laminated, and hot pressed at 170°C and 100 kg m^{-2} give a sheet with d of 1.45 μm. It had charpy impact strength 2 kg m^{-2} and bonding strength 10 kg mm^{-2}, which was pulverised to form 500 μm powders with good ability to remove moulding fins without scratching. The 100 parts polyalene 535 (ethylene–propylene–piene rubber) was mixed with MF 415 (melamine–formaldehyde resin) 30, N–660 (carbon black) 15, elastozinc (ZnO) 6.5, MBTS (thiazole) 1.2, Rm 98D (sulphur) 3, celogen 745 A (modified azodicarbonamide) 2, parts and other additive to develop a polymer blend for multipurpose uses. It was extruded as a solid rod, cured and blown to give foamed rubber[15] of 29.1 lbs/ft^3, compressive force deflection (50%) and 254 lbs/in^2 in compression set of 4.1%.

There has been a search for water based stove coating[16] materials; these were prepared by mixing water–reducible palm stearin alkyds with methylated formaldehyde–melamine copolymer at ratio of 1 to 9. The thermal gravimetric analysis (TGA) was used to estimate solid content of each of coatings and curing temperature to prevent thermal degradation. However the gloss of coating after cure was affected by oil length alkyd–melamine ratio and curing temperature but was found useful to assess the thermal properties.

Several amino resins[17], a good cross linking agent for acrylic resin coating were prepared from melamine (I), formaldehyde and isobutanal (II) by hydroxymethylation and etherification. The optimum reaction conditions were obtained for mole ratios of (I) to HCHO 1 : 6.6 at 90°C for 45 minutes and pH 6 to 6.5 in hydroxymethylation; and mole ratio of (I) to (II) 1 : 7. The reaction temperature was reflux temperature for 60 minutes and pH 4.8 to 5.1 in etherification. The amino resin with acrylic resin have been found to enhance lustre, hardness and adherence of acrylic resin coating superior to those of common butylated melamine resin coatings.

An admixture of a high range of water reducing agent have been selected from polyalkylollysulfonates, sulfonated melamine–formaldehyde resin derivatives[18], aromatic amino sulfonates and fly ash of particle size ≤ 20 μm. The cement compounds with above admixture were observed to give high water reducing rate, ability and segregation resistance to the composition. The coatings composed of a mixture of nonaqueous polymer dispersions[19] NAD (Nicotinamde Adenine Dinucleotide) solution, acrylic polyol melamine–formaldehyde resin have given a typical two phase system. Not only in liquid enamel but also in cross linked

films with discrete polymer particles bring out specific features in coating performance, especially in automotive metallic finishes to improve their rheol, mechanical properties and durability.

The polyester films[20] cured by MF resin were investigated by XPS paints containing polyester resin with low hydroxyl values, highly methylate MF and strong acid catalyst neutralized by volatile amines gave films surface of higher nitrogen concentration e.g. higher MF concentration. A flexible prepregnated[21] material for manufacture of more complex shapes without cracks, comprising ≥ 1 layers of a laminar carrier impregnated with an uncured resin e.g. melamine formaldehyde copolymer were seen to be of industrial significance. The carrier is a laminar porous polymer material e.g. open pore–polyethylene film or non–woven polyethylene, polyproylene, polyamide or polyester fibre. The elongation at the break of prepregnated and of separated impregnated laminar is > 10% and prepregnated form has been manufactured by impregnating a carrier with resin. Optionally in presence of a melting agent; drying (pre–curing) stack forming a shaped product and curing the composition contains an alkali solution resin, an acid generator, and methoxylated melamine formaldehyde crosslinking agent with OH value ≥ 10. The resistant image has been manufactured by applying above composition on a substrate drying, irradiating with an active radiation, heating and developing with an aqueous alkali solution. This composition shows a high sensitivity to active radiation e.g. UV, far–UV, X–ray and electron beam etc. and gives high resolution images on Ti or Si–nitride coated substrate.

The caprolactam–modified melamine resin[22] useful for coating was manufactured from a reaction mixture comprising 1 : 2 to 3 : 0.8, preferably 1 : 2 to 3.5 : 1 melamine–formaldehyde caprolactum mixture. Thus 160 kg of 37% formalin was alkalised at pH 8 to 9 with 10% aqueous NaOH, 82 kg. The malamine and 80 kg caprolactam were added and mixture refluxed to give a resin of viscosity (Ford cup 4) > 20 second, dry solids content > 60%, curing time (150°C) > 11 min, miscibility with water 1 : 1 to 7 and free formaldehyde content < 1%. The amphoteric interpenetrating phenolic aminoplast resins[23] (DHFA–8) have been synthesized by polycondensation of resorcinol; formaldehyde and melamine in pores of macro porous beads of cross–linked polystyrene. The DHFA–8 beads contain amine and phenol groups in interpenetrating structure. A curable, alkaline, melamine[24] modified phenol–formaldehyde resin was prepared from an initial phenol–formaldehyde resole resin containing 0.5 to 2.5% of the formaldehyde by scavenging formaldehyde with 1 to 12 parts of melamine for each 100 parts of the initial resin. Wherein a molar ratio of formaldehyde to melamine was 0.2 to 1.5 mole of formaldehyde for each mole of melamine to reduce free formaldehyde to < 70% of that in the initial resin. The modified resin was found storage stable, containing < 0.7% of free formaldehyde, and maintaining its stability under application conditions. An ammonium salt of a strong acid and additional water has been incorporated into melamine modified resin to provide a binder for binder treated fibreglass.

The melamine–urea formaldehyde resins[25] were obtained comprising addition of melamine to an aqueous precondensate of urea and formaldehyde. Where the HCHO:NH_2 ratio [F/ NH_2] was higher than 1.5, at pH 6 to 8 and temperature from 20 to 90°C and an amount of melamine was such that the content in final resin was 1 to 5%. The temperature was maintained from 80 to 103°C at pH of 6.5 to 7.8 for 5 to 15 minutes, then at pH 7.2 to 7.5 while cooling to 40 to 60°C and adjusting urea and water contents within 30 minutes so as to attain 0.45 to 0.85 ratio of F/NH_2. After cooling the contents an adjustment of final pH at 8 to 10, an alkanolamine, selected from triethanolamine (TEA), methyldiethanolamine and diethylmethylamine were used for final pH adjustment. Interestingly through out the process the sodium metabisulfite and methanol was added to the reaction medium to maintain final contents in the resin at or below 5%, respectively. Such kind of resins have been found suitable for use as thermosetting aminoplast for impregnating and were prepared by placing in a reactor containing an aqueous solution of formaldehyde and sodium metabisulfite in a ratio of 15 to 58 mol. The pH was adjusted to about 7 by addition of aqueous NaOH and then urea (2.4 mol) and melamine (0.476 mol), the temperature was brought to 98°C at 6.5 pH for 10 minutes. An aqueous formic acid has been used to adjust 4.6 pH and condensation was allowed to proceed to an end point, at which the pH was adjusted to 7.2 and the temperature to 60°C. The urea was added over 30 mins under cooling to 20°C and the 8.7 pH was adjusted with aqueous NaOH or TEA (triethanolamine). The resins thus obtained have been found to posses a composition of urea 33.7%, formaldehyde 23.3%, melamine 3% and F/NH_2 from 40 and 42%, viscosity from 40 and 42 mpa/second, gelation temperature from 140°C and 146°C. Their stability was found for 28 and 30 days at 20°C and 7 to 12 days at 30°C for NaOH and TEA resins, respectively. The aqueous 10 to 40% aqueous urea–formaldehyde–melamine resins[26] solutions were manufactured by (a) refluxing a urea HCHO–melamine mixture with HCHO–NH_2 groups in a mole ratio of 0.85 to 1.15 for 15 minutes at pH 7 to 8.5.(b) Polycondensing of the mixture at pH 5 to 6.5 and 70 to 100°C for 20 to 60 minutes and stopping polycondensation by cooling to 60 to 80°C at pH 7–8. (c) Adding formaldehyde, urea, and melamine in 0.6 to 0.9 mole ratio of HCHO and NH_2, and continuing polycondensation for 30 to 120 minutes at pH 8 to 10 and 70 to 100°C. The wood shaving[27] were coated with water repellents of high melting fatty acids, amides and hot pressed to prepare ply boards and thus, lauan chips were pulverised and mixed with an adhesive containing formaldehyde melamine urea copolymer and ethylene bis–stearyl amide and used to prepare particleboard. Similarly a synthetic resin product was coated with an aqueous dispersion containing sumitex resin (melamine–urea–formaldehyde initial condensate) 6, poly solution AZ 505 (reactive acrylate emulsion) 4, colloidal silica 7.5 to 1.4 and titanium oxide 10% dried were heated and irradiated with UV to attain good hydrophillicity (water contact angle 0°C). After storage in dark, the product was irradiatiated again with UV to recover the hydrophillicity. The composition, especially for bonding for plywood, comprises a thermosetting resin of a copolymer of formaldehyde and urea, melamine or methylol melamine and a water absorbing polymer[28], which shows absorbing of 20 times of water, based on its

weight have been manufactured. Thus a compound having initial adhesion of 2.22 kg cm^{-2} was made from 100 g oshikla resin 601 (formaldehyde–melamine–urea copolymer) containing KI, Gel 201 K–F21, water 10 and powder wheat 15 g.

The micro capsule type adhesives useful as a component in reactive or solvent–reactivating adhesives comprise an adhesive core and capsule[29] walls were formed by the reaction of aminoplasts and polyisocyanates. Thus 150 mL xylene containing 60 g coronate–L was dispersed in a solution of formaldehyde–melamine copolymer resins. Aqueous solution 100, formaldehyde–urea copolymer of (I), 158, water 62 triethanolamine, 1, 10% sodium alkyl benzenesulfonate aqueous solution 3 g, and 10% citric acid aqueous solution stirred at 30° for 20 hrs for preparation of micro capsules of average particle of 5–20 μ diameter were undertaken. The neoprene rubber 100, a phenolic rubber 100, a phenolic resin 1, a coumarone resin 1 and microcapsules 20 parts were mixed for a micro capsule–type adhesive. The moldings[30] were manufactured by mixing inorganic cellular particles with binders comprising isocyanates and ≥ 1 compound chosen from amino resins, phenolic resins, acrylic emulsions, and/or starch hot pressing and drying. Thus Shirasu balloon 100, formaldehyde–urea–melamine copolymer 13, U–loid UR 4000, 3 parts and water 8 parts were mixed, spreaded in a frame, pressed at 80^oC and dried at 180^oC for manufacture of a 9 mm material thickness. It was left at 20^oC and 60% relative humid for 1 week to have density 0.38 cm^{-3}, thickness 9.02 mm and bending strength 221N cm^{-2} at 25 and 185 N cm^{-2} at 40^oC.

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