Preparation and Characterization of a Low-Formaldehyde-Emission Methylol Urea/Triethanolamine Copolymer Composite

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ABSTRACT: A low-formaldehyde-emission methylol urea/triethanolamine composite was synthesized through *in situ* esterification of formaldehyde with triethanolamine and subsequent copolymerization of the synthesized polyester with methylol urea. The effects of the addition of triethanolamine to the polymerization process on some physical properties of the synthesized copolymer were evaluated. The copolymer was characterized with IR spectroscopy and macrophase-separation techniques. At a given triethanolamine concentration, the composite exhibited macrophase-separation behavior between that of pure methylol urea and pure polyester. IR spectra showed the presence of the polyester moiety in the composite. The values of the moisture uptake, formaldehyde emission, melting point, and elongation at break of the copolymer were within acceptable levels required in the coating industry. Therefore, the methylol urea/polyester copolymer resin could have potential as a binder in the coating industry. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 645–653, 2010

Key words: density; films; networks; phase separation; polyesters

INTRODUCTION

Amino resins are thermosetting polymers largely used in many industrial applications. Urea formaldehyde accounts for over 80% of the amino resins used, whereas melamine makes up most of the rest.[1–3] The principal attractions of amino resins are their water solubility before curing, which allows easy application to many materials; their colorlessness for unlimited colorability with dyes and pigments, their low cost, and their outstanding hardness and heat resistance.[1–3]

Despite their many attractive features, the acceptance of amino resins as universal materials in many engineering areas, especially in the coating industry (e.g., paint binders), is impeded by some of their inherent qualities, such as brittleness, poor water resistance, and formaldehyde emissions.[1,4] In our previous work,[5] we recorded a substantial reduction in the moisture uptake and formaldehyde emissions from a urea formaldehyde resin through a one-step synthetic route. However, the problem of resin hardness remained.

The importance of synthesizing polymers containing moieties capable of participating in polymerization reactions during or after polymerization reactions continues to increase in today's coating industry. The primary reason for this is that producing coating systems with lower contents of volatile organic compounds is imperative.[6] However, the desire to lower the content of volatile organic compounds sometimes generates some side effects. One approach to solving these problems is to use polymers containing moieties that may be an integral part of the polymer chain or be a byproduct capable of participating in other desirable reactions.[6]

In this work, we aimed to further reduce formaldehyde emission levels and introduce flexibility into the urea formaldehyde resin through *in situ* esterification of emitted CH_2O and copolymerization of methylol urea (MU) with triethanolamine (TEA). The obtained copolymer may have potential as a thermoset coating agent.

EXPERIMENTAL

Resin synthesis

MU was prepared according to the procedure outlined by Chen et al.[7] with 0.2 g of sodium dihydrogen phosphate as the catalyst. The pH of the solution was adjusted to 6 with $0.5M$ H_2SO_4 and $1.0M$ NaOH solutions. The solution was then heated in a thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h, after which the sample was removed and kept at room temperature (30°C). The obtained resin was used for the copolymerization reaction after 24 h.

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Copolymerization of MU with TEA

Gelation of the copolymer composite was obtained through the polymerization of the MU resin with various concentrations of TEA (0–10%). The mixture was stirred vigorously and allowed to stay for 24 h at room temperature (30°C) before film casting. Films of the different methylol urea/triethanolamine (MUT) copolymer composites were prepared with a solution-casting method;[8] 10 mL of each sample was cast onto a Petri dish and allowed to cure for 7 days at 30°C.

Determination of the viscosity

The solution viscosity was investigated with respect to the concentration of TEA according to the previous method reported by Barminas and Osemeahon.[5] A Phywe 100-mL graduated glass macrosyringe (Phywem, Gottingen, Germany) was used for the measurement. The apparatus was standardized with a 20% (w/v) sucrose solution with a viscosity of 2.0×10^{-3} N s m^{-2} at 30°C. The viscosity of the resin was evaluated with respect to that of the standard sucrose solution at 30°C. Five different readings were taken for each sample, and the average value was calculated.

Determination of the density, turbidity, melting point, and refractive index

The aforementioned properties were determined according to the method of the Association of Official Analytical Chemists.[9] The densities of the different resins films were determined with the weight of a known volume of the resin inside a density bottle with a Mettler AT 400 (GmbH, Greifensee, Switzerland) weighing balance. The turbidity of the resin solutions was determined with a Hanna model H193703 (Villafranca Padovana, Italy) microprocessor turbidity meter. The melting of different film samples was determined with a Galenkamp model MFB600-010F (Loughborough, UK) melting-point apparatus. The refractive indices of solutions of the resin were determined with an Abbe refractometer (Bellinglam & Stanley, Tunbridge Wells Kent, UK). Five readings were taken for each sample, and mean values were calculated for each of the aforementioned parameters.

Determination of the moisture uptake

The moisture uptake of the different resin films (1.0 g) was determined gravimetrically. Known weights of each of the samples were introduced into a damp and humid desiccator containing a saturated solution of sodium chloride. The wet weights of each sample were then monitored until a constant weight was obtained. The difference between the wet weight and dry weight of each sample was then recorded as the moisture intake by the resin. The moisture determination was repeated five times, and the results are reported as mean values.

Determination of the formaldehyde emission

A formaldehyde emission test was performed with the standard 2-h desiccator test.[10] The resin was poured into a mold made from aluminum foil with dimensions of 69.6 mm × 126.5 mm and a thickness of 1.2 mm before the test.[11] The mold and its contents were then allowed to equilibrate for 24 h, after which it was placed inside a desiccator along with 25.0 mL of water, which absorbed the formaldehyde that was emitted. The setup was allowed to remain for 2 h, after which 25 mL of water was removed and analyzed for its formaldehyde content. The amount of absorbed formaldehyde was obtained from a standard calibration curve derived by a refractometric technique with an Abbe refractometer.

Determination of the tensile properties

The breaking load and elongation at break were determined with the method reported by Wang and Gen.[11] A sample with dimensions of 50 × 10 × 1.2 mm^3 was loaded into an Instron (USA) model 1026 machine at a cramp rate of 20 mm/min. The process was repeated five times for each sample, and the average elongation of the samples was taken and expressed as the percentage increase in length.
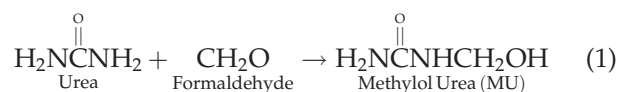
Melting-point differential macroseparation technique

To investigate the effect of the introduction of TEA into MU, a melting-point differential macrophase separation technique was developed. In this technique, mixtures of MU containing different concentrations of TEA were introduced into a porcelain dish in a ratio of 95:5. The dish with its contents was transferred into an oven set at 120°C for curing. The mixture was removed periodically from the oven and stirred until the mixture gelled and finally solidified. The temperature was then raised to 150°C and left for 5 min, after which the sample was removed and cooled for macro-observation.
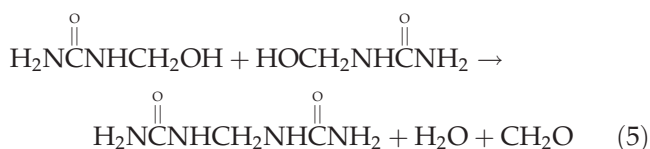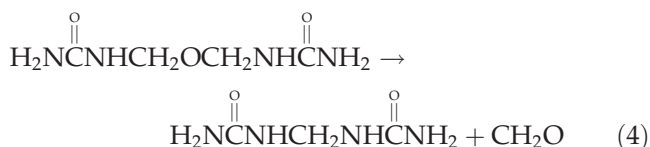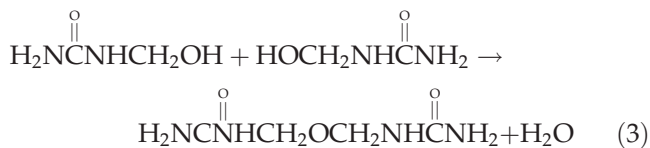
RESULTS AND DISCUSSION

MUT copolymer chemistry

The reaction for the formation of MU is as follows:

$$\underset{\text{Urea}}{H_2N\overset{\overset{O}{\|}}{C}NH_2} + \underset{\text{Formaldehyde}}{CH_2O} \rightarrow \underset{\text{Methylol Urea (MU)}}{H_2N\overset{\overset{O}{\|}}{C}NHCH_2OH} \quad (1)$$

During curing, the amino resin undergoes cross-linking as result of the following condensation reactions:

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2OH + H_2N\overset{O}{\overset{||}{C}}NH_2 \rightarrow$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2HN\overset{O}{\overset{||}{C}}NH_2 + H_2O \qquad (2)$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2OH + HOCH_2NH\overset{O}{\overset{||}{C}}NH_2 \rightarrow$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2OCH_2NH\overset{O}{\overset{||}{C}}NH_2 + H_2O \qquad (3)$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2OCH_2NH\overset{O}{\overset{||}{C}}NH_2 \rightarrow$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2NH\overset{O}{\overset{||}{C}}NH_2 + CH_2O \qquad (4)$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2OH + HOCH_2NH\overset{O}{\overset{||}{C}}NH_2 \rightarrow$$

$$H_2N\overset{O}{\overset{||}{C}}NHCH_2NH\overset{O}{\overset{||}{C}}NH_2 + H_2O + CH_2O \qquad (5)$$
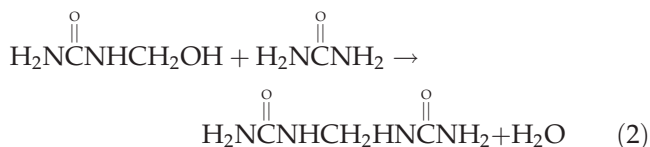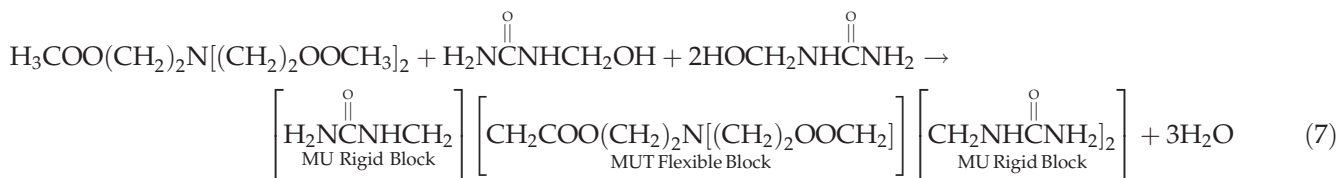
Therefore, during the condensation reactions of MU resins into polymer chains, formaldehyde (i.e.,

H_2CO) is released [reactions (4) and (5)] and eventually emitted as a toxicant into the surroundings.[1] However, this formaldehyde contains carbonyl groups, just like the isocyanate ($-N=C=O$) used in the formation of polyurethanes. Analogously, it may be possible for the carbonyl groups in formaldehyde to react with polyols, starting a sequence of gelation reactions leading to the formation of the MUT copolymer composite. More importantly, the hazardous formaldehyde will be captured from the system by the polyols through *in situ* esterification:

$$\underset{\text{Formaldehyde}}{3(H_2CO)} + \underset{\text{Triethanolamine}}{OH(CH_2)_2N[(CH_2)_2OH]_2} \rightarrow$$

$$\underset{\text{Polyester (Soft block)}}{H_3COO(CH_2)_2N[(CH_2)_2OOCH_3]_2} \qquad (6)$$
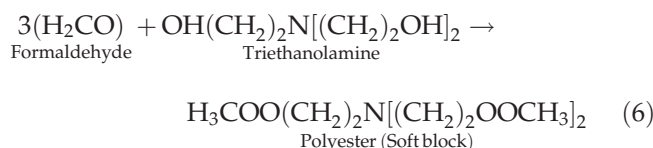
The produced polyester will be incorporated into the backbone of the MU as a copolymer resin through the copolymerization process, and segmented flexibility will be introduced into the urea formaldehyde resin (a situation akin to polyurethane):

$$H_3COO(CH_2)_2N[(CH_2)_2OOCH_3]_2 + H_2N\overset{O}{\overset{||}{C}}NHCH_2OH + 2HOCH_2NH\overset{O}{\overset{||}{C}}NH_2 \rightarrow$$

$$\left[\underset{\text{MU Rigid Block}}{H_2N\overset{O}{\overset{||}{C}}NHCH_2}\right]\left[\underset{\text{MUT Flexible Block}}{CH_2COO(CH_2)_2N[(CH_2)_2OOCH_2]}\right]\left[\underset{\text{MU Rigid Block}}{CH_2NH\overset{O}{\overset{||}{C}}NH_2]_2}\right] + 3H_2O \qquad (7)$$

Copolymer morphology

Reactions (6) and (7) could contribute to the solid-state morphology and physical properties of the copolymer. These physical properties are a function of the cellular structure and phase-separation morphology of the copolymer. These two factors are related to segmented flexibility, chain entanglement, interchain interactions, and crosslinking.[12] The morphology of the solid portion of MUT was investigated with a macroseparation technique and IR spectroscopy.

Figure 1 shows the macrophase-separation behavior of the MUT composite. Figure 1(a) shows the phase-separation behavior of the MUT copolymer. Two phases were observed; the whitish phase was soft and foamlike, whereas the other segment was transparent and hard, just like the parent MU resin. The water in reaction (7) acted as a hard-segment-domain plasticizer. The phase separation occurred when the concentration of the hard segment

exceeded a system-dependent solubility limit, leading to the formation of MU microdomains. Hence, the polyester matrix contained dispersed MU microdomains as aggregates (macrophases) and also provided the covalent crosslinking points. Also, hydrogen bonds may have formed readily between the proton donor NH— groups of the MU rigid block and its electron-donor carbonyl groups.[12]

The reaction temperature of 150°C was not high enough to melt the hard MU segments, the melting point of which was measured at 263°C. This shows that the MU hard segments cohesively bonded the soft polyester segments covalently. This could be achieved through strong hydrogen-bonding interactions, which provided the cohesiveness of the microdomain.

Figure 1(b) shows the effect of the TEA concentration on the macrostructure of the cured films of the MUT copolymer. The soft segment (whitish phase) increased with an increase in the TEA concentration.
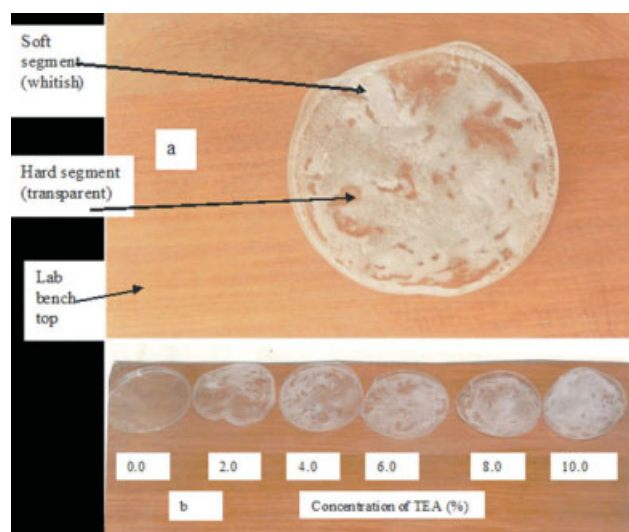
Figure 1 Macrophase-separation behavior of the MUT copolymer composite: (a) hard and soft segments and (b) effects of the TEA concentration on the phase separation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This could be attributed to the availability of the polyester chains for copolymerization with MU as the concentration of TEA increased.[12]

IR spectroscopy

Figure 2 shows the spectra of the MU resin and MUT copolymer composite. In the MU spectrum, the broad band stretching from 3600 to 2800 cm^{-1} is due to the O—H group from MU, which overlapped with those of water and the N—H group of MU.[13,14] This broadening of these absorption frequencies is an indication of complexity in the structure of the copolymer due to the entrapment of impurities such as traces of water and formaldehyde that could readily form hydrogen bonds with —NH, NH$_2$, or —CH$_2$OH.

The 1086-cm^{-1} peak is due to the C—O—C group, and the weak band around 1740 cm^{-1} is assigned to the C=O group.[13,15] New peaks at 984, 1159, and 1446 cm^{-1} and around 2855 cm^{-1} in the spectra of MUT are due to O—H deformation of the oligoester, the stretching vibration of C—O, —CH$_2$—scissoring and CH$_3$ asymmetric bending deformation, and C—H attachment to the ester group, respectively.[16,17]

In a comparison of MU and MUT, the broad OH band present in MU was replaced with new peaks in the MUT spectra. The weak peak around 1971 cm^{-1} in MU became very strong in MUT, and the appearance of peaks around 3733 and 3849 cm^{-1} MUT was also new. The reduction in the OH band in MUT could be attributed to an increase in the consumption of the OH groups in MU due to the copolymerization reaction between MU and polyester.[16] This development might have been brought about by the introduction of the new functional group (—OO—) by the copolymerization process, which thereby consumed most of the MU OH groups. The copolymerization reaction between the
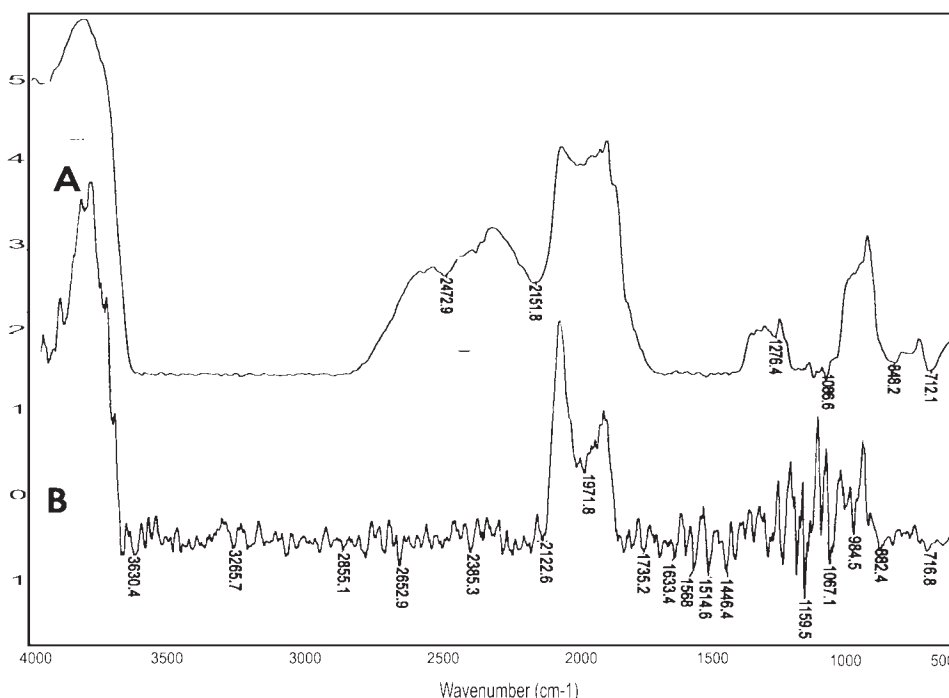

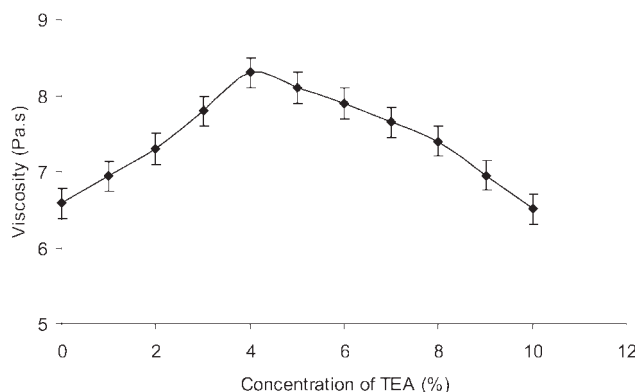**Figure 2** IR spectra of (a) MU and (b) MUT.

Figure 3 Effect of the TEA concentration on the viscosity of MU.

MU resin and the polyester could be explained by the drastic reduction in the wave number of the OH group of MU from 3600 to 2800 cm^{-1}.

The appearance of the —CH$_2$— peak is due to the presence of the relatively long alkyl chains from the polyester. Perhaps the presence of the O—H deformation of the oligoester at 984 cm^{-1}, the C—O stretching vibration at 1159 cm^{-1}, the C=O stretching vibration at 1740 cm^{-1}, C—H attachment to the ester group at 2855 cm^{-1}, and the —CH$_2$ scissoring at 1446 cm^{-1} confirm the existence of the polyester moiety in MUT. The lack of a sharp and strong band at 3600 cm^{-1} differentiates the assigned O—H deformation band of the oligoester from that of isolated trace water.

Viscosity

Figure 3 presents the effect of TEA on the viscosity of the MU resin. A large increase in the viscosity was observed as the TEA concentration increased from 0 to 4%. This was followed by a gradual decrease in the viscosity with a further increase in the concentration of TEA. This type of result can be explained on the basis of the segmental factor of the resin. Between 0 and 4% TEA, the MU or hard segment formed the continuous phase, and the soft segments were dispersed in the matrix of the hard segments. This was caused by strong interchain association forming large aggregates with large hydrodynamic volumes; hence, the high solution viscosity was observed.

Between 4 and 10% TEA, the soft segments formed the continuous phase, and the hard segments were dispersed in the matrix of the soft segments, notably producing a smaller viscosity increase. This was probably caused by the propensity of MU molecules to form intramolecular associations enhancing the formation of MU microdomains. In the intermediate zone (4% TEA), the copolymer

resin was characterized by viscosity properties different from those of both pure components.[18] Hence, the differences in the viscosity as the TEA percentage increased are attributable to the hydrogen bonds available for the disruption of the hard-segment domains. These physical network structures could contribute significantly to the rheological properties and, consequently, to the overall properties of the copolymer in different applications.

Refractive index

Gloss is an important quality factor of many coating products. The gloss of paint coatings with or without pigments is, among other things, a function of the refractive index of the surface.[19] Figure 4 shows the influence of the TEA concentration on the refractive index of the MU resin. The refractive index of the resin increased with an increase in the TEA concentration, reaching a maximum value at 4% TEA, after which a decrease in the refractive index was observed with an increase in the TEA concentration. This observation suggests that the aggregates which formed reached a maximum size at 4% TEA, after which dissociation occurred, forming resins with differences in their molecular features and orientations.[12,20]

Density

The density of paint has a profound influence on factors such as pigment dispersion, brushability, flow, leveling, and sagging.[4] The influence of the TEA concentration on the density of the MU resin is shown in Figure 5. The graph indicates an initial increase in the density of the resin with an increase in the TEA concentration up to 4% and then a decrease in the density with a further increase in the TEA concentration. A possible reason for this type of behavior may be due to the segmental factor, which gave rise to resins with different ratios of
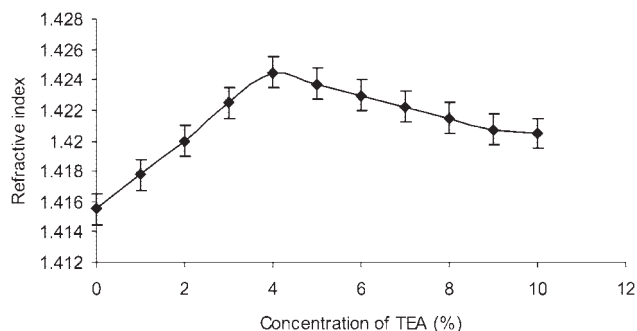

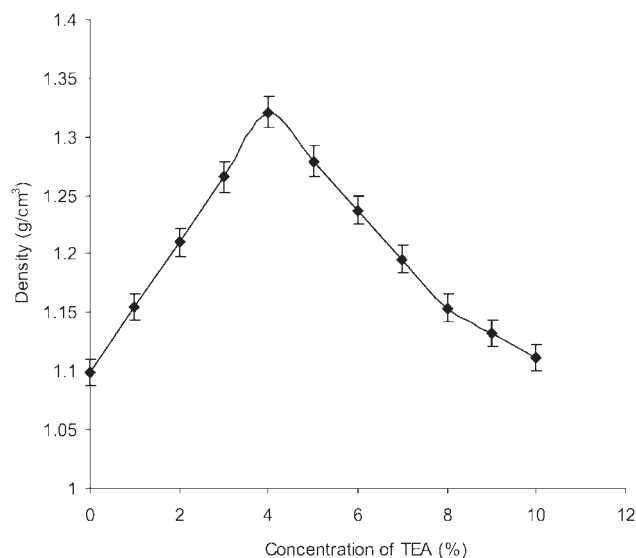**Figure 4** Effect of the TEA concentration on the refractive index of MU.

Figure 5 Effect of the TEA concentration on the density of MU.

hard and soft segments. This in turn influenced the packing nature of the resin molecules.[12,19]

Melting point

The melting point of a polymer has a direct bearing on its thermal properties.[21] It is related to the molecular weight, degree of crosslinking, and level of rigidity of the polymer.[15] In the case of the coating industry, the melting point of a binder is related to its thermal resistance and its brittleness. Figure 6 shows the effect of the TEA concentration on the melting point of the MU resin. The melting point of the MU resin decreased sharply with an increase in the TEA concentration. This trend can be attributed to the increase in the proportion of the polyester (soft segment) in the copolymer resin;[12] this suggests that macromolecular aggregates among MU microdomains were weakened in the polyester, and this resulted in lowering of the melting point. Aliphatic
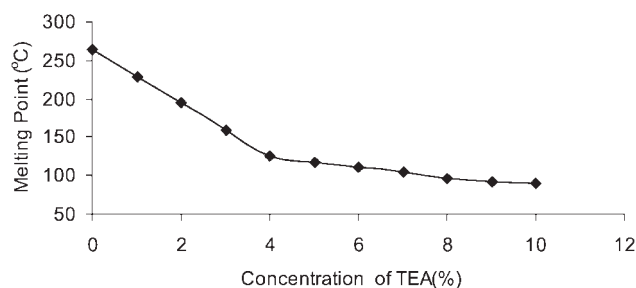

Figure 6 Effect of the TEA concentration on the melting point of MU.
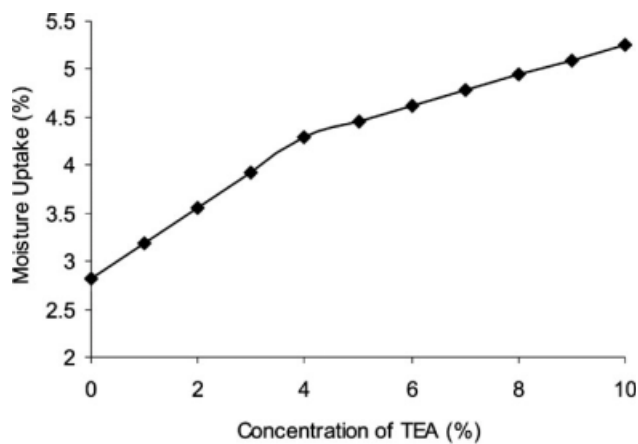
Figure 7 Effect of the TEA concentration on the moisture uptake of MU.

polyesters have low transition temperatures and are generally amorphous or have low melting points.[12]

Moisture uptake

Water uptake by polymers affects vital properties of polymer materials, such as physical, mechanical, and structural properties.[22,23] Figure 7 presents the effect of the TEA concentration on the moisture uptake of the copolymer. The copolymer exhibited a relatively sharp increase between TEA concentrations of 0 and 4%, and this was followed by a gradual increase from 4 to 10%. The observed trend may be due to both the segmental factor and the progressive increase in the OH groups in the system with an increase in the TEA concentration.[12] The gradual increase in the polyester segment with an increase in the TEA concentration resulted in resins with differences in the chain topology, molecular-size holes in the polymer, morphology, and crosslinked density.[22,24] This result further stressed the destabilizing effect of TEA on MU aggregates.
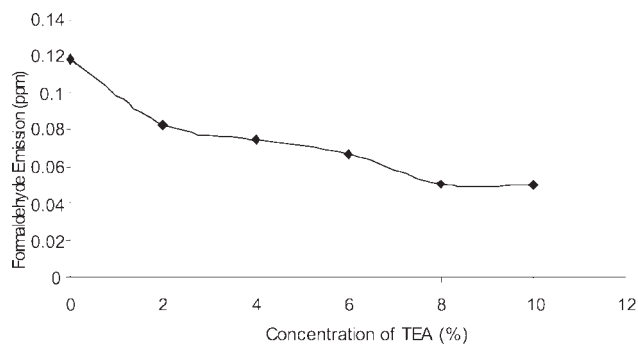

Figure 8 Effect of the TEA concentration on the formaldehyde emission of MU.

TABLE I
Effect of the TEA Concentration on the Tensile Strength and Elongation at Break of MU

TEA concentration (%)	Strength (kg/cm^2)	Elongation (%)
0	0.165 ± 0.002	85.01 ± 0.21
2	0.035 ± 0.001	135.02 ± 0.31
4	0.032 ± 0.001	240.02 ± 0.12
6	0.030 ± 0.001	220.04 ± 0.23
8	0.027 ± 0.001	180.05 ± 0.33
10	0.021 ± 0.001	160.11 ± 0.45

The values are means plus or minus the standard deviation (n = 5).

Formaldehyde emission

The emission of hazardous formaldehyde during curing is one of the major disadvantages of urea formaldehyde resins.[2,10,23] Hence, the reduction of this pollutant is an important environmental requirement. Figure 8 shows the effect of the TEA concentration on the formaldehyde emissions of MU. The formaldehyde emissions of MUT decreased with an increase in the TEA concentration. A plausible reason for this trend could be the conversion of the generated formaldehyde into polyester and subsequent copolymerization of the polyester with MU.

Tensile properties

The effect of the TEA concentration on the tensile properties of MU is shown in Table I. The tensile strength decreased with an increase in the TEA concentration, whereas the elongation at break increased as the TEA concentration increased from 0 to 4%, and this was followed by a gradual decrease with a further increase in the TEA concentration. This result is in agreement with similar work on polyurethane,[12] and it is due to the progressive increase in the molecular weight of the soft segment with respect to the hard segment.

The increase in the elongation at break shown with the increase in the TEA concentration was due to the weaker interchain attractive forces, which allowed an increase in chain slippage and disentanglement.[12] The molecular weight of the soft segment had a marked influence on the final elastomer properties, and increasing the molecular weight with respect to the hard segment produced a fall in the modulus and an increase in the elongation at break. This can be explained by the increase in flexibility and relative reduction in highly polar hard-segment attractions.[12] The decrease in the elongation at break from 4 to 10% observed in this experiment was due to the high molecular weight of the soft segment.

Comparison of some physical properties of the MUT copolymer and other resins

Table II compares some physical properties of some conventional urea formaldehydes with the urea formaldehyde/polyester copolymer resin obtained in this work. The moisture uptake was reduced from 18 to 4.3%, the melting point was reduced from 200 to 125°C, the formaldehyde was reduced from 0.70 to 0.074 ppm, and the density was reduced from 1.1764 to 1.1554 g/cm^3. These results indicate that the urea formaldehyde/polyester copolymer presented a resin with relatively very low moisture uptake and formaldehyde emissions. It also suggests that urea formaldehyde was softened with respect to the very hard and brittle resin obtained previously.[1] The reduction in density is also positive to the coating industry.[25]

Table III compares some physical properties of the MU/polyester copolymer resin and some commercial binders. The table indicates that the viscosity, melting point, moisture uptake, and elongation at break were all within the levels of traditional paint binders. This experiment also suggests that the problems of poor water resistance, hardness, and brittleness associated with conventional urea formaldehyde[4] can be addressed through the copolymerization of MU with the produced polyester.

TABLE II
Comparison of Some Physical Properties of the Urea Formaldehyde/Polyester Copolymer and the Conventional Urea Formaldehyde Resin

Property	MUT copolymer	Urea formaldehyde	Reference
Moisture uptake (%)	4.30 ± 0.10	18	Ajayi et al.[26]
Melting point (°C)	125.11 ± 2.05	200	Ajayi et al.[26]
Formaldehyde emission	0.074 ± 0.002	0.70	Kim[10]
Density (g/cm^3)	1.1554 ± 0.0013	1.1764	Ajayi[26]

The values are means plus or minus the standard deviation (n = 5).

TABLE III
Comparison of Some Physical Properties of the MU/Polyester Copolymer Film and Films from Other Paint Binders

Type of resin	Physical properties						Reference
	Viscosity (N s m^{-2})	Refractive index	Density (g/cm^3)	Melting point (°C)	Moisture uptake (%)	Elongation (%)	
MU/polyester copolymer	8.30 ± 0.02	1.4245 ± 0.0002	1.1554 ± 0.0013	125.11 ± 2.05	4.30 ± 0.10	240.02 ± 0.12	This study
Epoxy-based divinyl ester	0.8	38.0	ND	1.04	197	ND	Gawdzik and Matynia[27]
Styrene-modified epoxy	72	ND	ND	ND	200	ND	Yoon and McGrath[28]
Epoxy fumerate resins	0.96	45.0	ND	1.07	110	ND	Gawdzik et al.[29]
Whey protein isolate biopolymer	ND	ND	1.4838	ND	ND	ND	Trezza and Krochta[19]
Aromatic amine-modified polyethylene	ND	ND	ND	0.96	133	ND	Starostina et al.[30]
Silicone-modified styrene/butyl acrylate copolymer latex	ND	ND	ND	ND	ND	8.6	Wu et al.[31]
Rubber seed oil modified alkyd resins	24	3.11	ND	0.95	ND	ND	Aigbodion et al.[32]
Epoxy resins	ND	ND	ND	ND	101	0.04	Hu et al.[33]
Aqueous polyurethane	ND	ND	ND	ND	ND	17.2	Lee and Kim[34]

ND = not determined.

CONCLUSIONS

Esterification of formaldehyde with a polyol was successfully carried out to form a polyester polymer. The copolymerization of MU and the polyester in the presence of various concentrations of TEA produced a copolymer composite with a considerable reduction of formaldehyde emissions. Overall, the presence of polyester segments controlled the properties of the copolymer. The values of the moisture uptake, formaldehyde emissions, melting point, and elongation at break obtained from this experiment were within acceptable levels required in the coating industry. Therefore, this MU polyester copolymer resin appears to be a potential candidate as a binder for the coating industry.

References

1. Conner, H. A. In Encyclopedia of Polymeric Materials; Salamone, J. C.; Clapol, J.; Demby, A.; Aller, M., Eds.; CRC: Boca Raton, FL, 1996; Vol. 2, p 8495.
2. Pizzi, A.; Beaujean, M.; Zhao, C.; Properzi, M.; Huang, Z. J Appl Polym Sci 2001, 84, 2561.
3. Updegraff, H. I. In Encyclopedia of Polymer Science and Engineering; Kroschwitz, I.; Mark, H. F.; Bikales, N. M.; Olerberger, C. G.; Menges, G., Eds.; Wiley: New York, 1990; Vol 1, p 752.
4. Lowel, H. J. In Encyclopedia of Polymer Science and Engineering; Kroschwitz, J. I.; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1990; Vol. 3, p 615.
5. Barminas, J. T.; Osemeahon, S. A. Eur J Sci Res 2007, 16, 160.
6. Trumbo, D.; Mole, I.; Travino, E. B.; Denbrink, V. M. J Appl Polym Sci 2001, 82, 1030.
7. Chen, C.; Lue, J.; Yen, C. J Appl Polym Sci 2001, 83, 1242.
8. Mirmohseni, A.; Hassanzadeh, V. J Appl Polym Sci 2000, 79, 1062.
9. Official Methods of Analysis of AOAC International, 17th ed.; Horwitz, W., Ed.; Association of Official Analytical Chemists: Gaithersburg, MD, 2000.
10. Kim, G. M. J Appl Polym Sci 2001, 80, 2800.
11. Wang, H.; Gen, C. J Appl Polym Sci 2002, 84, 797.
12. Hepburn, C. Polyurethane Elastomers; Applied Sciences: Essex, United Kingdom, 1982; p 3.
13. Ahmad, S.; Ashraf, S. M.; Hasnat, A.; Yadav, S.; Jamal, A. J Appl Polym Sci 2001, 82, 1855.
14. Gan, S.; Tan, B. J Appl Polym Sci 2001, 80, 2309.
15. Park, H.; Yang, I.; Wu, J.; Kim, M.; Hahm, H. K.; Rhee, H. J Appl Polym Sci 2001, 81, 1614.
16. Diakaumakos, D. C.; Jones, N. F.; Ye, H.; Shen, C. W. J Appl Polym Sci 2001, 83, 1317.
17. Mohammed, A. H.; Bardam, M. B.; Aglan, A. H. J Appl Polym Sci 2001, 80, 286.
18. Lopez, M. A.; Biagotti, J.; Kenny, J. M. J Appl Polym Sci 2001, 81, 1.
19. Sekaran, G.; Thamizharasi, S.; Ramasami, T. J Appl Polym Sci 2001, 81, 156.
20. Trezza, A. T.; Krochta, J. M. J Appl Polym Sci 2001, 79, 2221.
21. Bindu, L. R.; Nair, C. P.; Nina, K. N. J Appl Polym Sci 2001, 80, 1664.
22. Nogueira, P. C.; Ramirez, A.; Torres, M. I.; Abad, J.; Cano, I.; Lopez-Bueno, I.; Barral, L. J Appl Polym Sci 2001, 80, 71.
23. El-Naggar, A. M.; Kandeel, K. A.; Khafaga, M. R.; Zahran, A. H. J Appl Polym Sci 2001, 82, 2869.

24. Lu, G. M.; Shim, J. M.; Kim, W. S. J Appl Polym Sci 2001, 81, 2253.
25. Gupta, S.; Mendon, K. S.; Thames, F. S. J Appl Polym Sci 2001, 82, 1718.
26. Ajayi, J. O.; Omizegba, F. I.; Barminas, J. T.; Osemeahon, S. A. Eur J Sci Res 2005, 4, 21.
27. Gawdzik, B.; Matynia, T. J Appl Polym Sci 2001, 81, 2062.
28. Yoon, T.; McGrath, J. E. J Appl Polym Sci 2001, 80, 1504.
29. Gawdzik, B.; Matynia, T.; Osypiuk, J. J Appl Polym Sci 2002, 79, 1201.
30. Starostina, A. I.; Stoyanov, O. V.; Bogdanova, S. A.; Deberdeev, R. J. A.; Kurnosor, V. V.; Zaikov, G. E. J Appl Polym Sci 2001, 79, 388.
31. Wu, Y.; Duan, H.; Yu, Y.; Zhang, C. J Appl Polym Sci 2000, 83, 333.
32. Aigbodion, I. A.; Pilla, C. K. S. J Appl Polym Sci 2001, 79, 2431.
33. Hu, X.; Fan, J.; Yue, C. Y. J Appl Polym Sci 2001, 80, 2437.
34. Lee, J. S.; Kim, B. K. J Appl Polym Sci 2001, 82, 1315.