

Full Length Research Paper

Development of amino resin for paint formulation: Copolymerization of methylol urea with polyester

Osemeahon, S. A. and Barminas, J. T.

Department of Chemistry, Federal University of Technology, Yola, P. M. B. 2076 Yola, Nigeria.

Accepted 19 April, 2007

In our continuous efforts to develop a paint binder from amino resin, a low formaldehyde emission methylol urea-triethanolamine (MUT) composite was synthesized through *in situ* esterification of formaldehyde with triethanolamine (TEA) and subsequent copolymerization of the synthesized polyester with methylol urea. The effects of addition of TEA on the polymerization process on some physical properties of the synthesized copolymer were evaluated. The copolymer was characterized by IR spectroscopy and macro phase separation techniques. At a given TEA concentration, the composite exhibited macro phase separation behavior between that of pure methylol urea and pure polyester. The IR spectra show the presence of the polyester moiety in the composite. The values of moisture uptake, formaldehyde emission, melting point and elongation at break of the copolymer were within the acceptable levels required in the coating industry. Therefore, the methylol urea/polyester copolymer resin could be a potential candidate as a binder for the coating industry.

Key words: Methylol urea-triethanolamine copolymer, flexibility, formaldehyde emission, copolymerization, methylol urea, esterification, tensile properties.

INTRODUCTION

Amino resins are thermosetting polymers that are largely used in many industrial applications. Urea formaldehyde accounts for over 80% of amino resins used while melamine makes up for most of the rest (Barminas and Osemeahon, 2006; Conner, 1996; Pizzi et al., 2001; Updegraff, 1990). The principal attractions of amino resins are their water solubility before cure which allows easy application to many materials; colorless, for unlimited colorability with dyes and pigments, low cost, outstanding hardness and heat resistance (Conner, 1996; Pizzi et al., 2001).

Despite possessing many attractive features, the acceptance of amino resins as universal material in many engineering areas especially in the coating industry as paint binders is impeded by some of its inherent qualities such as brittleness, poor water resistance and formaldehyde emission (Osemeahon and Barminas, 2006a; Conner, 1996; Lowel, 1990). In our previous work we recorded a substantial reduction in moisture uptake and

formaldehyde emission from urea formaldehyde resin through one step process (OSP) synthetic route (Barminas and Osemeahon, 2007). But the problem of resin hardness remained.

The importance of synthesizing polymers containing moieties capable of participating in polymerization reactions continue to increase in today's coating industry. The primary reason for this is that producing coating systems with lower volatile organic compounds (VOCs) content is imperative (Trumbo et al., 2001). However, the desire to lower (VOC) content some times generates some side effects. One approach to solve these problems is to use polymers containing moieties which may be an integral part of the polymer chain or be a byproduct capable of participating in other desirable reactions (Trumbo et al., 2001).

In the present work, we aim at further reduction of formaldehyde emission level and introduce flexibility into the urea formaldehyde resin through *insitu* esterification of the emitted formaldehyde and copolymerization of methylol urea with triethanolamine. The copolymer obtained may find potential application as a thermoset coating agent.

*Corresponding author E-mail: sundayosemeahon@yahoo.com.
Tel: + 234 080 5347 9527.

MATERIALS AND METHODS

Materials

Urea, Formaldehyde, sodium dehydrogenate phosphate, sulphuric acid, sodium hydroxide, sucrose and Triethanolamine were obtained from BDH.

Resin synthesis

Methylol urea was prepared according to the procedure outlined by Chen et al. (2001), using 0.2 g of sodium dihydrogen phosphate as catalyst. The pH of the solution was adjusted to 6 using 0.5 M H₂SO₄ and 1.0 M 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 resin obtained was used for the copolymerization reaction after 24 h.

Copolymerization of methylol urea with triethanolamine

Gelation of the copolymer composite was obtained through polymerization of methylol urea resin with various concentrations of Triethanolamine (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 cured on petri dishes by using solution casting method (Mirmohseni and Hassanzadeh, 2000) and curing allowed for seven days at 30°C.

Determination of viscosity

The solution viscosity was investigated with respect to concentration of TEA according to the previous method (Barminas and Osemeahon, 2006). Five different readings were taken for each sample and the mean value recorded.

Determination of density, turbidity, melting point and refractive Index

The above properties were determined according to AOAC method (AOAC, 2000). The densities of the different resins were determined by taking the weight of a known volume of resin inside a density bottle using Metler At400 weighing balance. Five readings were made for each sample and the mean value recorded. The turbidity of resin solutions were determined by using Hanna micro-processor turbidity meter model H193703. The melting of the different film samples were determined by using Galenkamp melting point apparatus model MFB600-010F. The refractive index of the resin solutions which is the ratio of the Sin of the angle of incident to the Sin of the angle of refraction were determined by using Abbe refractometer. With respect to turbidity, melting point and refractive index, triplicate measurements were made for each sample and mean value reported.

Determination of moisture uptake

The moisture uptake of the different resin films was determined gravimetrically. Known weights of each of the samples were introduced into a damp humid desiccator containing a saturated solution of sodium chloride. The wet weight of each sample was 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 (Barminas and Osemeahon, 2006). All determinations were performed in triplicate and results reported as mean value.

Determination of formaldehyde emission

Formaldehyde emission test was performed by using the standard 2 h desiccator test (Kim, 2001). The evaluation of the absorbed formaldehyde by 25.0 ml water was obtained from a standard calibration curve derived from refractometric technique using Abbe refractometer. The resin was poured into a mold made from aluminium foil with a dimension of 69.6 mm x 126.5 mm and thickness of 1.2 mm prior to the test (Wang and Gen, 2002). Measurements were made in triplicates and results reported as means ± S.D.

Determination of tensile properties

The breaking load and elongation at break were determined by using a standard method (Wang and Gen, 2002). A sample whose dimension is 50 x 10 x 1.2 mm was loaded into an Instron Machine Model 1026 at cramp rate of 20 mm/min. The process was repeated five times for each sample and the average elongation of the sample taken and expressed as the percentage increase in length.

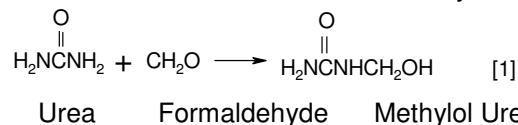
Melting point differential macro separation technique

To investigate the effect of introduction of triethanolamine into methylol urea, a melting point differential macrophase separation technique was developed. In this technique, mixtures of methylol urea containing different concentrations of triethanolamine (0-10%) were introduced into different porcelain dish. The dish with its content was transferred into an oven set at 120°C for curing. The mixture was removed periodical 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 observation. The experiment was also repeated three times.

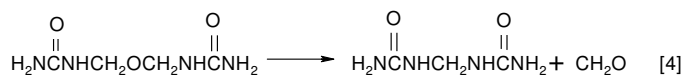
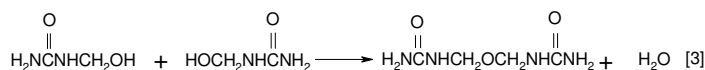
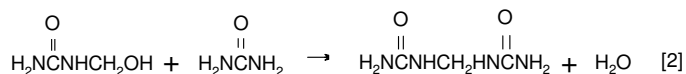
RESULTS AND DISCUSSION

MUT copolymer chemistry

The reaction for the formation of methylol urea is given by



During curing, the amino resin undergoes crosslinking as result of the following condensation reactions (1):



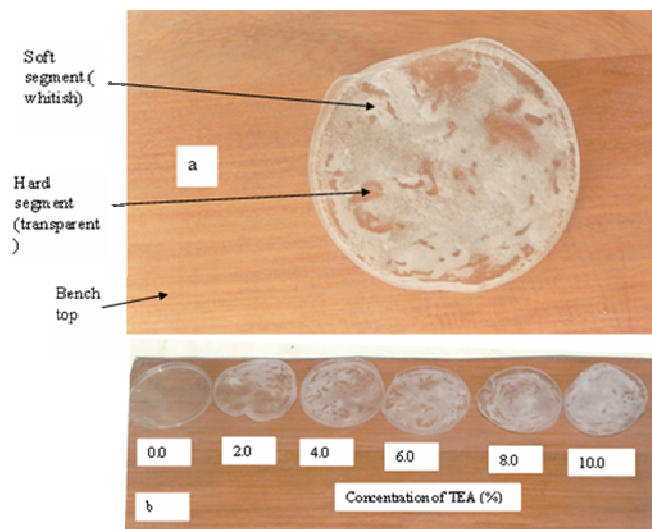
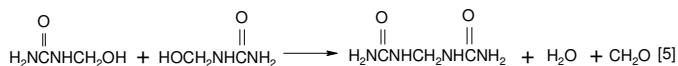
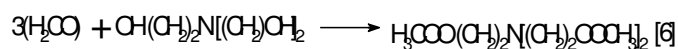


Figure 1. Macrophase separation behaviour of MUT copolymer composite [(a) hard and soft segments. (b) Effect of TEA concentration on phase separation].

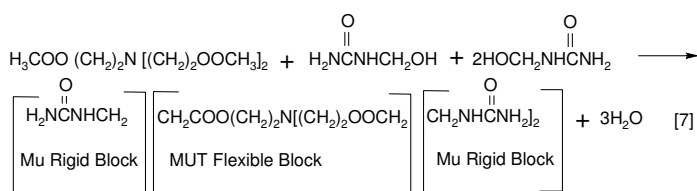


Therefore during the condensation reactions of methylol urea resins into polymer chains, formaldehyde CH_2O was released (equations 4 and 5) and eventually emitted as a toxicant to the surroundings [1]. However, this CH_2O contains carbonyl group just like isocyanate ($-\text{N}=\text{C}=\text{O}$) used in the formation of polyurethanes. In analogy, it may be possible for the carbonyl group in CH_2O to react with polyols in TEA to start a sequence of reactions leading to the formation of MUT copolymer composite. More importantly the hazardous formaldehyde will be captured from the system by the polyol through *insitu* esterification:



Formaldehyde Triethanolamine Polyester (Soft block)

The produced polyester will be incorporated into the backbone of the methylol urea as a copolymer resin through copolymerization process and segmented flexibility will be introduced into urea formaldehyde resin, a situation akin to polyurethane.



Copolymer morphology

Reactions in equations 6 and 7 could contribute to 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 and chain entanglement; through inter chain interaction and crosslinking (Hepburn, 1982). The morphology which comprises of the solid portion of MUT was investigated by macro separation technique and IR spectroscopy.

Figure 1 shows the macrophase separation behavior of MUT composite. Figure 1a shows the phase separation behaviour of MUT copolymer. Two phases were observed; the whitish phase was soft and foam-like while the other segment was transparent and hard just like the parent MU resin. The water in equation 7 acted as a hard segment domain plasticizer. The phase separation occurred when the concentration of the hard segment exceeds 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 cross-linking points. Also hydrogen bonds may be formed readily between the proton donor NH- groups of the MU rigid block and its electron donor carbonyl groups (Hepburn, 1982; Osemeahon and Barminas, 2006a).

The reaction temperature of 150°C was not enough to melt the hard methylol urea segments whose melting point was obtained at $263^\circ\text{C} \pm \text{S.D}$. This shows that the MU hard segments cohesively bonded the soft polyester segments covalently. This can be achieved through strong hydrogen bonding interactions which provide the cohesiveness of the microdomain.

Figure 1b shows the effect of triethanolamine concentration on the macro structure of the cured films of MUT copolymer. It was observed that the soft segment (whitish phase) increased with increase in triethanolamine concentration. This is attributed to the availability of the polyester chains for copolymerization with methylol urea as the concentration of triethanolamine increases (Hepburn, 1982; Osemeahon and Barminas, 2006a).

IR spectroscopy

Figure 2 shows the spectra of MU resin and MUT copolymer composite. In the MU spectra, the broad band stretching from 3600 through 2800 cm^{-1} is due to the O-H group from methylol urea which overlapped with that of water and the N-H group of the methylol urea (Ahmad et al., 2001; Gan and Tan, 2001). The 1086 cm^{-1} peak is due to C-O-C group and the weak band around 1740 cm^{-1} is assigned to C=O group (Ahmad et al., 2001; Pizzi et al., 2001). New peaks at 984 , 1159 , 1446 and around 2855 cm^{-1} in the spectra of MUT are due to O-H deforma-

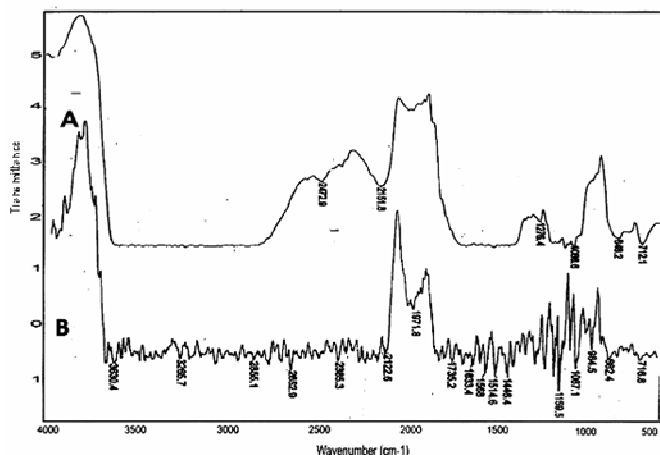


Figure 2. IR spectra of (A), MU resin and (B) MUT copolymer composite.

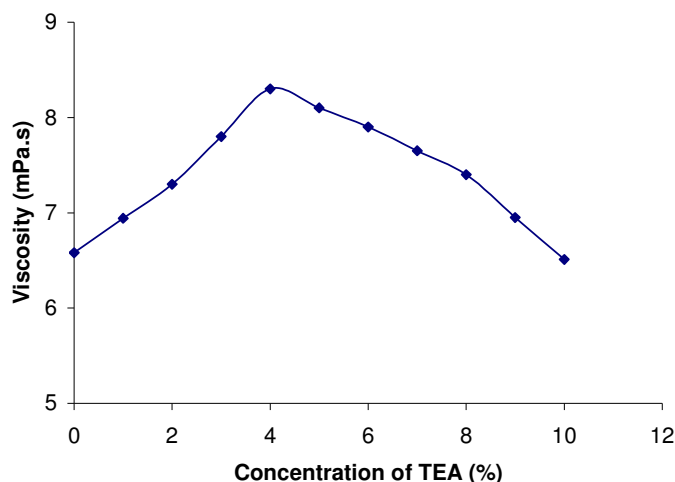


Figure 3. Effect of TEA on the viscosity of methylol urea (Results are mean values of five determinations).

tion of oligoester, stretching vibration of C-O, $-\text{CH}_2$ -scissoring and CH_3 asymmetric bending deformation and C-H attachment to ester group, respectively (Diakaumakos et al., 2001; Mohammed et al., 2001).

In comparing 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 are also new. The reduction in the OH band in MUT can be attributed to an increase in the consumption of the OH groups in methylol urea due to copolymerization reaction between methylol urea and polyester (Diakaumakos et al., 2001). This development might have been brought about by the introduction of the new functional group ($-\text{OO}-$) by the copolymerization process thereby consuming most of the MU OH groups. The copolymerization reaction between the methylol urea

resin and the polyester could be accounted for by the drastic reduction in wave numbers of OH group of the methylol urea at 3600 through 2800 cm^{-1} band.

The appearance of $-\text{CH}_2-$ peak is due to the presence of the relatively long alkyl chains from the polyester. Perhaps the presence of the O-H deformation of oligoester at 984 cm^{-1} , C-O stretching vibration at 1159 cm^{-1} , C=O stretching vibration at 1740 cm^{-1} , C-H attachment to ester group at 2855 cm^{-1} and the $-\text{CH}_2$ scissoring at 1446 cm^{-1} confirm existence of polyester moiety in MUT.

Viscosity

Figure 3 presents the effect of TEA on the viscosity of methylol urea resin. A large increase in viscosity was observed from 0–4% TEA concentration. This was followed by a gradual decrease in viscosity with further increase in the concentration of TEA. This type of result can be explained on the basis of segmental factor of the resin (Barminas and Osemeahon, 2006). Between 0–4% TEA, the methylol urea 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 inter-chain association forming large aggregates with large hydrodynamic volumes; hence the high solution viscosity observed.

Between 4 – 10% TEA, the soft segment formed the continuous phase and the hard segments were dispersed in the matrix of the soft segments notably giving smaller viscosity increase. This is probably caused by the propensity of MU molecules to form intramolecular associations that may enhance the formation of MU microdomains. In the intermediate zone (4% TEA), the copolymer resin is characterized by physical properties different from both pure components (Lopez et al., 2001; Osemeahon and Barminas, 2006b). Hence the differences in the viscosity as the % TEA increases may be attributed to the hydrogen bonds available for 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 pigment is among other things a function of the refractive index of the surface (Sekararan et al., 2001). Figure 4 shows the influence of TEA concentration on the refractive index of methylol urea resin. The refractive index of the resin increases with increase in TEA concentration reaching maximum value at 4% TEA, after which a decrease in refractive index was observed with increase in TEA concentration. This observation suggests that the

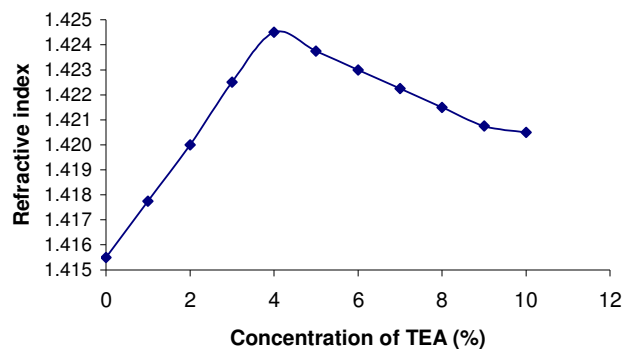


Figure 4. Effect of TEA concentration on the refractive index of methylol urea (values are means of triplicate measurements).

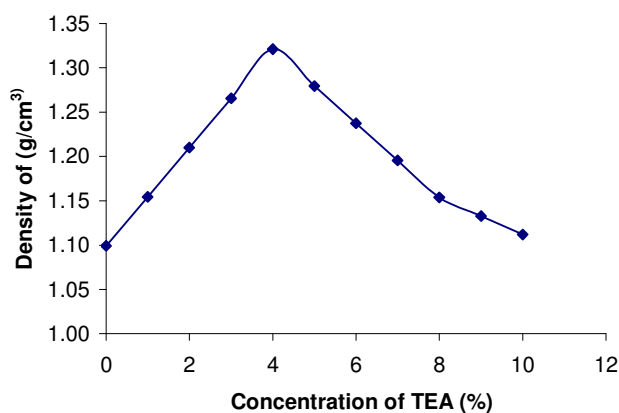


Figure 5. Effect of TEA Concentration on the density of methylol urea (values are mean values of five determinations).

aggregates formed reached a maximum size at 4 % TEA, after which dissociation occurred forming resins with differences in molecular features and orientations (Barminas and Osemeahon, 2006; Trezza and Krochta, 2001).

Density

The density of paint has a profound influence on factors such as pigment dispersion, brushability of paint, flow, leveling and sagging (Barminas and Osemeahon, 2007; Lowel, 1990). The influence of TEA concentration on the density of methylol urea resin is shown in Figure 5. The graph indicates an initial increase in density of the resin with increase in TEA concentration attaining a maximum at 4% TEA concentration. The possible reason for this type of behaviour may be due to the segmental factor which gave rise to resins with different ratios of hard and soft segments. This in turn influences the packing nature of resin molecules (Barminas and Osemeahon, 2007; Sekaran et al., 2001).

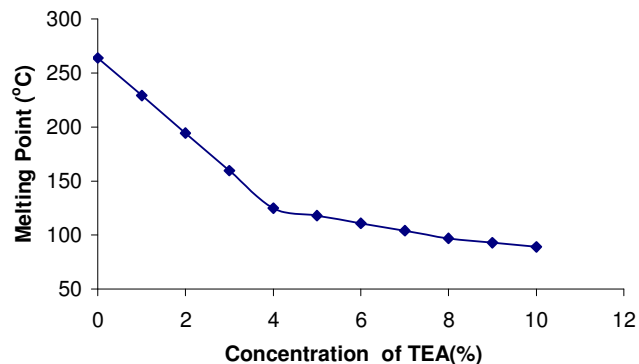


Figure 6. Effect of TEA concentration on the melting point of methylol urea (values are means of triplicate determinations)

Melting Point

The melting point of a polymer has a direct bearing on its thermal property (Bindu et al., 2001). It is related to its molecular weight, degree of crosslinking and the level of rigidity of the polymer (Park et al., 2001). In the case of the coating industry, the melting point of a binder is related to its thermal resistance as well as to its brittility. Figure 6 shows the effect of TEA concentration on the melting point of methylol urea resin. It is observed that the melting point of methylol urea resin decreased sharply with increase in TEA concentration. This trend can be attributed to the increase in the proportion of the polyester (soft segment) in the copolymer resin (Hepburn, 1982; Osemeahon and Barminas, 2006b), suggesting that macromolecular aggregations among MU microdomains are weakened in the polyester resulting in lowering of the melting point. Generally aliphatic polyesters have low transition temperatures and are amorphous and have low melting points (Hepburn, 1982).

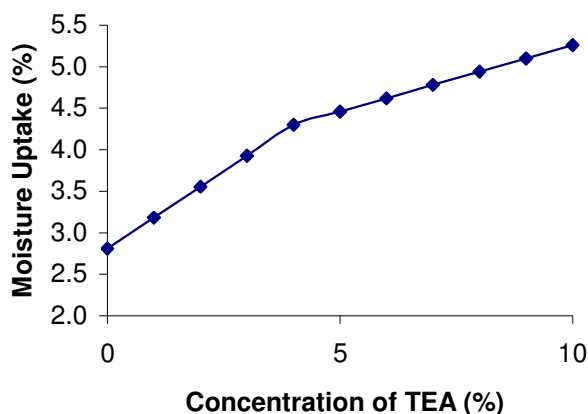
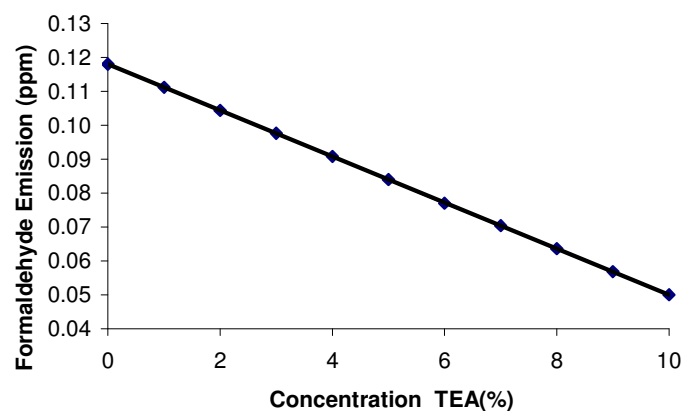
Moisture uptake

Water uptake by polymers affects vital properties of the polymer material such as physical, mechanical and structural properties (Lu and Kim, 2001; Nogueira et al., 2001). From Figure 7 the effect of TEA concentration on the moisture uptake of the copolymer is presented. The copolymer exhibits a relatively sharp increase between 0 – 4% TEA concentration and followed by a gradual increase from 4 – 10% TEA concentration. The observed trend may be due to both segmental factor and the progressive increase in OH group in the system with increase in TEA concentration (Hepburn, 1982; Barminas and Osemeahon, 2007). The gradual increase in polyester segment with increase in TEA concentration resulted in resins with differences in chain topology, molecular size holes in the polymer, morphology and crosslinked density (Osemeahon and Barminas, 2006a; Lu and Kim, 2001; Nogueira et al., 2001). This result further stressed

Table 1. Effect of TEA concentration on the tensile strength and elongation at break of methylol urea.

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

Values are mean ± S.D (n =3).

**Figure 7.** Effect of TEA concentration on the moisture uptake of methylol urea (values are means of triplicate determinations).**Figure 8.** Effect of concentration of TEA (%) on the formaldehyde emission of methylol urea (values are means of triplicate determinations).

the destabilizing effect of TEA on MU aggregates.

Formaldehyde emission

The emission of the hazardous formaldehyde during cure is one of the major disadvantages of the application of urea formaldehyde resins (Barminas and Osemeahon, 2007; EL-Naggar et al., 2001; Kim, 2001). Hence the reduction of this pollutant is an important environmental requirement. Figure 8 shows the effect of TEA concentration on the formaldehyde emission of methylol urea. The result shows that the formaldehyde emission of the MUT decreased with increase in TEA concentration. The plausible reason for this trend could be the conversion of the generated formaldehyde into polyester and subsequent copolymerization of the polyester with methylol urea.

Tensile properties

The effect of TEA concentration on the tensile properties of methylol urea resin is shown in Table 1. The result

show that the tensile strength decreases with increase in TEA concentration while the elongation at break increased from 0 – 4% of TEA concentration followed by a gradual decrease with further increase in TEA concentration. This result is in agreement with similar work on polyurethane (Osemeahon and Barminas, 2006a; Hepburn, 1982) and, it is due to the progressive increase in molecular weight of the soft segment relative to the hard segment.

The increase in elongation at break shown with increase in TEA concentration is due to the weaker interchain attractive forces, which allow increase in chain slippage and disentanglement (Osemeahon and Barminas, 2006a). The molecular weight of the soft segment has a marked influence over the final elastomeric properties, and increasing the molecular weight relative to the hard segment producing a fall in modulus and an increase in the elongation at break. This is explained by the increase in flexibility and relative reduction in highly polar hard segment attractions (Hepburn, 1982). The decrease in elongation at break from 4 – 10% observe in this experiment is due to the high molecular weight of the soft segment.

Table 2. Comparison of some physical properties of urea formaldehyde/polyester copolymer (MUT) and the convectional urea formaldehyde (UF) resin.

Property	MUT copolymer	UF (Reference)
Moisture Uptake (%)	4.30±0.10	18 (Ajayi et al.,2005)
Melting Point (°C)	125.11±2.05	200 (Ajayi et al., 2005)
Formaldehyde emission (ppm)	0.074±0.002	0.70 (Kim, 2001)
Density (g/cm ³)	1.1554±0.0013	1.1764 (Ajayi, 2001)

Table 3. Comparison of some physical properties of methylol urea/polyester copolymer film with films from other paint binders.

Types of Resin	Gel Time (h)	Viscosity (Pa.s)	Refractive Index	Density (g/cm ³)	Melting Point (°C)	Moisture Uptake (%)	Literature
Methylol Urea/Polyester Copolymer	8.31±0.64	1.4245±0.003	1.1554±0.0013	125.11±2.05	4.30±0.10	240.02±1.15	This study
Epoxy-based Divinyl Ester	0.8	38.0	ND	1.04	197	ND	Gawdzik and Matynia (2001)
Styrene Modified Epoxy	72	ND	ND	ND	200	ND	Yoon and Mcgrath, 2001
Epoxyfumerate Resins	0.96	45.0	ND	1.07	110	ND	Gawdzik et al. (2001)
Whey Protein Isolate biopolymer	ND	ND	1.4838	ND	ND	ND	Trezza and Krochta (2001)
Aromatic amines-modified polyethylene	ND	ND	ND	0.96	133	ND	Starostina et al. (2001)
Silicone-Modified styrene-butyl acrylate copolymer latex	ND	ND	ND	ND	ND	8.6	Wu et al. (2000)
Rubber Seed oil modified alkyd resins	24	3.11	ND	0.95	ND	ND	Aigbodion and Pilla (2001)
Epoxy Resins	ND	ND	ND	ND	101	0.04	Hu et al. (2001)
Aqueous Polyurethane	ND	ND	ND	ND	ND	17.2	Lee and Kim (2001)

ND: Not Determined.

Comparison of some physical properties of MUT copolymer with other resins

Table 2 compares some physical properties of some conventional urea formaldehyde with urea formaldehyde/polyester copolymer resin obtain in this work. It can be observed that the moisture uptake is reduced from 18–4.3%, melting point from 200–125°C, formaldehyde from 0.70–0.074 ppm and the density from 1.1764 – 1.1554 g/cm³. This result indicates that urea formaldehyde/polyester copolymer is presenting a resin with relatively very low moisture uptake and formaldehyde emission. It also suggests that urea formaldehyde is being softened as against the very hard and brittle resin obtained previously (Barminas and Osemeahon, 2007). The reduction in density is also a positive value to the coating industry (Gupta, 2001).

Table 3 compares some physical properties of methylol urea/polyester copolymer resin with some commercial binders. The table indicates that the viscosity, melting point, moisture uptake and elongation at break are all within the levels of traditional paint binders. This experiment also suggest that the problems of formaldehyde emission, poor water resistance, hardness and brittleness associated with the conventional urea formaldehyde (Lowel, 1990) is been addressed through the copolymerization of methylol urea with the produced polyester.

Conclusion

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

REFERENCES

- Ahmad S, Ashraf SM, Hasnat A, Yadav S, Jamal A (2001). Studies on Urethane-Modified Alumina – Filled Polyesteramide Anticorrosive Coatings Cured at Ambient Temperature J. Appl. Polym. Sci. 82: 1855 – 1865.
- Aigbodion IA, Pilla CKS (2001). Synthesis and Molecular Weight Characterization of Rubber Seed Oil – Modified Alkyd Resins. J. Appl. Polym. Sci. 79: 2431 – 2438.
- Ajayi JO, Omizegba FI, Barminas JT, Osemeahon SA (2005). Reactive Dye – Resin Complexation of Cellulose Substrates, Eur. J. Sci. Res. 4: 21 – 32.
- AOAC (2000). Official Method of Analysis International, (Horwitz, W., Editor). Gaithersburg Mongland, USA, 17th edition Vol. 1, 41: 1-68
- Barminas JT, Osemeahon SA (2007): Novel Development of Amino Resins for Paint Formulation. 1. Effect of pH on a New Synthetic Route. Eur. J. Sci. Res. 16: 160-173.
- Barminas JT, Osemeahon SA (2006): Development of Amino Resins for Paint Formulation. 11.Effect of Temperature on New Synthetic Route. Eur. J. Sci. Res. 14: 489-499.
- Bindu LR, Nair CP, Nina KN (2001) Phenolic Resins with Phenyl Maleimide Function: Thermal Characteristic and Laminate Composite Properties. J. Appl. Polym. Sci. 80: 1664 – 1674.
- Chen C, Lue J, Yen C (2001). Insitu Pultrusion of Urea – Formaldehyde Matrix Composite. 1. Processibility, Kinetic Analysis, and Dynamic Mechanical properties. J. Appl. Polym. Sci., 83: 1242 – 1251.
- Conner HA (1996). Urea – formaldehyde Adhesive Resins. In: Encyclopedia of Polymeric Material (Joseph, C., Salamone, J. Clapol, Demby, A. and Aller, M.) Vol.2, pp 8495 -8500.
- Diakaumakos DC, Jones NF, Ye H, Shen CW (2001): High – Solids Mar Resistance Clear Coats Prepared from an Isophthalate – based Oligoester and Melamine Resin. Study and Characterization of Mar Resistance with Scanning Probe Microscope Method, J. Appl. Polym. Sci., 83: 1317 – 1333.
- EI-Naggar AM, Kandeel KA, Khafaga MR, Zahran AH (2001). Control of Resin Release from Particle Boards by Gamma Irradiation. 1. Thermal Decomposition Behaviour and Structural Morphology. J. Appl. Polym. Sci. 82: 2869 – 2881.
- Gan S, Tan B (2001): FTIR Studies of the Curing Reactions of Palm Oil Alkyd-m-elamine enamels, J. Appl. Polym. Sci. 80: 2309-2315.
- Gawdzik B, Matynia T (2001). Synthesis and Modification of Epoxy-based Divinyl Ester Resin. J. Appl. Polym. Sci, 81: 2062 – 2067.
- Gawdzik B, Matynia T, Osypiuk J (2000). Influence of TDI concentration on the Properties of Unsaturated Polyester Resins. J. Appl. Polym. Sci. 79:1201– 1206.
- Gupta S, Mendon KS, thames F S. (2001). Application of Epoxidized and Hydroxy-Fluoroester Pendent Secondary High-Molecular-Weight Guayule Rubber in Coating, J. Appl. Polym. Sci., 82: 1718 – 1724.
- Hepburn C (1982). Polyurethane Elastomers, Applied Science Publisher, Essex England Pp. 3.
- Kim GM (2001). Examination of Selected Synthesis Parameters for Wood Adhesive – type Urea – Formaldehyde Resins by CNMR Spectroscopy. J. Appl. Polym. Sci. 80: 2800 – 2814.
- Lee JS, Kim BK (2001). Modification of Aqueous Polyurethane via Latex AB Crosslinked Polymers. J. Appl. Polym. Sci. 82: 1315 – 1322.
- Lowel HJ (1990). Coatings. In: Encyclopedia of Polymer Science and Engineering, (Kroschwitz, J. I., Mark, H. F., Bikales NM, Overberger CG, Menges G.) Vol. 3, pp. 615.
- Lu M, Kim S (2001). Unsaturated Polyester Resins Based on Recycled PET: Preparation and Curing Behavior. J. Appl. Polym. Sci. 80: 1052 – 1057.
- Mirmohseni A, Hassanzadeh V (2000). Application of Polymer – Coated Quartz Crystal Microbalance (QCM) as a Sensor for BTEX Compounds Vapours. J. Appl. Polym. Sci. 79: 1062 – 1065.
- Mohammed AH, Bardam MB, Aglan AH (2001). Laterborne Methylamine Adduct as Corrosion Inhibitor for Surface Coating. J. Appl. Polym. Sci. 80: 286 – 296.
- Nogueira PC, Ramirez A, Torres MI, Abad J, Cano I, Lopez-bueno, Barral L (2001). Effect of Water Sorption on the Structure and Mechanical Properties of An Epoxy Resin System. J. Appl. Polym. Sci. 80: 71 – 80.
- Osemeahon SA, Barminas JT (2006a). Properties of a low Viscosity Urea-Formaldehyde Resin Prepared through a New Synthetic Route. Bulletin of Pure and Applied Sciences. 25C: 67-76.
- Osemeahon SA, Barminas JT (2006b). A New Synthetic Route for Amino Resins for Paint Formulation: Effect of Sodium dihydrogen phosphate (NaHP) as catalyst. . Bulletin of Pure and Applied Sciences. 25C: 111-118.
- Park H, Yang I, Wu J, Kim M, Hahm HKKS, Rhee H (2001). Synthesis of Siliconacrylic Resins and their Applications to Supperweatherable Coatings. J. Appl. Polym. Sci. 81: 1614–1623.
- Pizzi A, Beaujean M, Zhao C, Properzi M, Z Huang (2001). Acetal – Induced Strength Increases and Lower Resin Content of MUF and Other Polycondensate Adhesives, J. Appl. Sci, 84: 2561 – 2571.
- Sekaran G, Thamizharasi S, Ramasami T (2001). Phsiochemical – Modified Polyphenol Impregnate. J. Appl. Polym. Sci. 81: 1567 –

- 1571.
- Starostina AI, Stoyanov OV, Bogdanova SA, Deberdeev RJA, Kurnosor VV, Zaikov GE (2001). Studies on the Surface Properties and the Adhesion to Metal of Polyethylene Coatings Modified with Primary Aromatic Amines. *J. Appl. Polym. Sci.* 79:388 – 397.
- Trezza AT, Krochta JM (2001). Specular Reflection, Gloss, Roughness and Surface Heterogeneity of Biopolymer Coatings *J. Appl. Polym. Sci.* 79: 2221 – 2229.
- Trumbo DI, Mole EB, Travino SA, Denbrink VM (2001): Copolymerization Behavior of 3 – Isopropyl- α -Dimethylbenzylamine and a Preliminary Evaluation of the Copolymer in Thermosetting Coatings, *J. Appl. Polym. Sci.*, 82: 1030 – 1039.
- Udegraff HI (1990). Amino Resins. In: *Encyclopedia of Polymer Science and Engineering* (Kroschwitz, I., Mark, H. F., Bikales NM, Olerberger CG, G Menges), Vol 1:752 – 763.
- Wang H, Gen C (2002). Synthesis of Anionic Water-Borne Polyurethane with Covalent Bond of a Reactive dye. *J. Appl. Polym. Sci.* 84: 797 – 805.
- Wu Y, Duan H, Yu Y, Zhang C (2000). Preparation and Performance in Paper Coating of Silicone – Modified Styrene – Butyl Acrylate Copolymer Latex. *J. Appl. Polym. Sci.* 83:333 – 336.
- Yoon T, Mcgrath JE (2001). Curing and Toughening of a Styrene-modified Epoxy Resin. *J. Appl. Polym. Sci.* 80: 1504 – 1513.