

Full Length Research Paper

Development of amino resin for emulsion paint formulation: reactive blending of methylol urea with soybean oil

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In this work, methylol urea resin (MUR) was reactively blended with various concentrations (0 - 35%) of soybean oil (SBO) in order to formulate a new two-component polymer system for application as a coating agent for emulsion paint formulation. Formaldehyde emission and some physical properties of the blended resin were evaluated. Moisture uptake and density decreased with increase in the SBO content in the blend. Elongation at break and viscosity also decreased initially before a gradual increase was observed as the SBO content increases. Refractive index, melting point and dry time initially increased but gradually decreased with increase in SBO content. The interactions between the two different polymers show that 25% of SBO was the optimal loading inclusion. The values of moisture uptake, formaldehyde emission, melting point and elongation at break which were 1.3%, 0.05 ppm, 120°C, and 140%, respectively, are within acceptable levels required in the coating industry. The advantages of this new system are low formaldehyde emission and water reduction characteristics. The polymer blend may therefore be recommended as binder for the coating industry.

Key words: Paint binder, amino resins, methylol urea, soybean oil, reactive blending.

INTRODUCTION

Polymer systems consisting of components with different properties are usually known to possess some advantages over the individual polymers. Amino resins are normally produced by reactions involving formaldehyde with amine functional compounds such as melamine and urea. With the exception of being used as crosslinking agent in some oil-based paint, urea formaldehyde cannot be used as a paint binder because of its inherent qualities such as brittleness, poor water resistance and formaldehyde emission (Conner, 1996; Lowel, 1990). However, for application in coatings, urea formaldehyde could be modified to satisfy some specific requirements for an emulsion paint formulation.

Blending is a powerful tool for tailoring the physical, chemical and mechanical properties of polymers products (Pizz et al., 2002; Manchado et al., 2001). By utilizing blends we can allow a polymer resin to cover a broad

range of applications that might otherwise be inaccessible. Rheological behavior and processability of polypropylene blends with rubber ethylene propylene diene terpolymer to improved toughness (Manchado et al., 2001; Xiano et al., 2002) have been studied. Also, work on the flame retardancy of cured epoxy resin with brominated cast oil and lowering of formaldehyde emission by lowering resin content of urea formaldehyde adhesive with acetals were subjects of previous investigations (Pizzi et al., 2002).

Soybean oil (SBO) is one of the most commonly consumed vegetable oils for several food processing and like any other oil or fat it is essentially triglyceride of a trihydral alcohol (glycerol) and fatty acids (Dale, 2004). It is polyunsaturated with three double bonds positioned at carbons 9, 12 and 15 along the 18 carbon aliphatic chains (Dale, 2004; Can et al., 2001). It is hydrophobic in nature and possesses functional groups that could be involved in chemical reactions, namely; the ester linkage, the carboxylic acid (COOH) group and the double bonds (Dale, 2004). Methylol urea resin (MUR) possesses hydroxyl (OH) functional group and this OH group is

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capable of undergoing esterification reaction with the COOH group of soybean oil. This might lead to a reduction in moisture uptake (due to the presence of hydrophobic soybean oil), formaldehyde emission (due to a reduction in amino resin loading inclusion) and an increase in softness and flexibility (due to increase in alkyl length) of methylol urea resin.

The aim of this experiment therefore, is to undertake reactive blending of methylol urea with soybean oil to form a low formaldehyde coating for possible coating applications especially as a paint binder for emulsion paint formulation.

EXPERIMENTAL

Methylol urea resin synthesis

Trimethylol urea was prepared by reacting one mole (6.0 g) of urea with three moles (24.3 ml) of 37% (w/v) formaldehyde using 0.2 g sodium dihydrogen phosphate (Chen et al., 2001). 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 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).

Blend preparation

Blending of methylol urea with soybean oil was done by preparing 5% soybean oil in methylol urea at room temperature (30°C). The solution was mixed thoroughly using magnetic stirrer. The above procedure was repeated at different soybean oil concentrations (5 - 35%) and the resulting blends analyzed. Films of the different resins obtained with various SBO concentrations (5 - 35%) were cast on Petri dishes by using solution casting method (Mirmohseni and hassanzadeh, 2000). The resins were then allowed to cure and set for seven days at 30°C. The physical properties of these films were investigated.

Determination of physical properties

The viscosity of the polymer blend was adopted from a previously outlined method (Barminas and Osemeahon, 2006). Other physical properties were determined according to standard procedures (AOAC, 2000). The density was determined by taking the weight of a known volume of resin inside a density bottle using Metler at 400 weighing balance. Five readings were made for each sample and average value calculated. The turbidity of resin samples were determined by using Hanna microprocessor 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 resin samples was determined by using Abbe refractometer.

The moisture uptake was obtained gravimetrically. Known weights of each of the samples were introduced into a 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 samples were then recorded as the moisture intake by resin. Triplicate determinations were performed for each sample and the average value calculated.

Determination of formaldehyde emission

Formaldehyde emission test was performed by using the standard 2 h desiccator test (Kim, 2001). The mold used made from aluminium foil with a recommended dimension of 69.6 mm x 126.5 mm (Kim, 2001) and thickness of 1.2 mm (Wang and Gen, 2002). The emitted formaldehyde was absorbed in 25.0 ml water and analyzed refractometric technique using Abbe refractometer. Triplicate samples were used and average value taken.

Tensile test and dry time measurement

Tensile properties were measured as described by Wang and Gen (2002) using Instron Testing Machine (Model 1026). In brief, resin films of dimension 50 mm long, 10 mm wider and 0.15 mm thick were brought to rupture at a clamp rate of 20 mm/min. A number of five runs were taken for each sample and the average elongation were taken and expressed as the percentage increase in length. The relative degree of cure was expressed in the form of dry time (dry to touch) which was measured by the qualitative finger marking test (Ali et al., 2001).

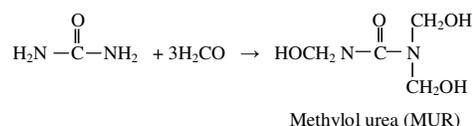
RESULTS AND DISCUSSION

IR spectra

The overlay IR spectra of pure methylol urea and its blend with SBO blend is shown in Figure 2. In the spectra of pure methylol urea, the broad band stretching from 3600 cm⁻¹ is due to the OH group from the methylol urea which however overlapped with that of water and the N-H group of methylol urea (Ahmad et al., 2001; Gan and Tan, 2001). The peak observed at 1086 cm⁻¹ is due to C-O-C group while the weak band around 1740 cm⁻¹ is due to C=O group (Ahmad et al., 2001 and Park et al., 2001). In the spectra of the two component polymer system, new peaks were recorded at 997, 1137, 1490 and around 2791–1855 cm⁻¹ which are due to O-H deformation of oligoester, stretching vibration of C-O, -CH₂- scissoring and CH₃-asymmetric bending deformation and C-H attachment of ester group, respectively (Diakaumakos et al., 2001; Mohammed et al., 2001).

The IR spectra of MUR/SBO blend indicate that the broad OH band present in pure methylol urea is almost disappeared while the bands at 1744 and 1444 cm⁻¹ in methylol urea spectra which characterize the carbonyl functional groups were shifted to 1660 and 1490 cm⁻¹ in polymer blend. The new peaks close to 997, 1052 and within 2791–2855 cm⁻¹ in the modified methylol urea indicate the presence of ester group. The drastic increase in the intensity of the 1490 cm⁻¹ peak signaled an increase in alkyl length due to the long alkyl group from SBO.

The addition of the formaldehyde to the amine groups for methylol urea used by the reaction of N-H across the C=O of the formaldehyde.



urea and SBO. In a dilute system, there are strong specific interactions and the complexes are isolated from each other with the formation of compact structure, which reduced the viscosity of the blend solution. However, as the blend concentration increased, the isolated complexes combined and lead to the formation of a gel-like intermolecular complex structure, which lead to the increase in the solution viscosity of the polymer blend system (Qi et al., 2002).

Refractive index

Gloss is an important quality factor of many coating products. The gloss of a coating with or without pigments is a function of refractive index of the surface, the angle

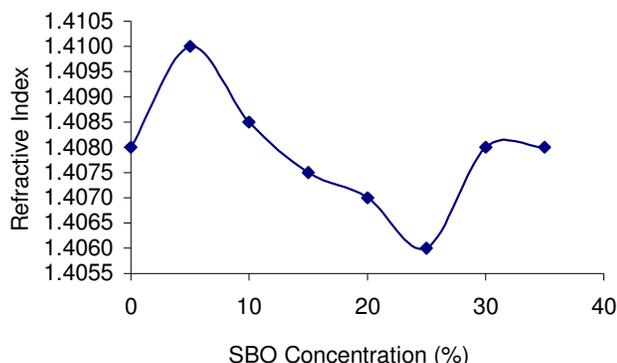


Figure 4. Effect of SBO concentration on the refractive index of methylol urea.

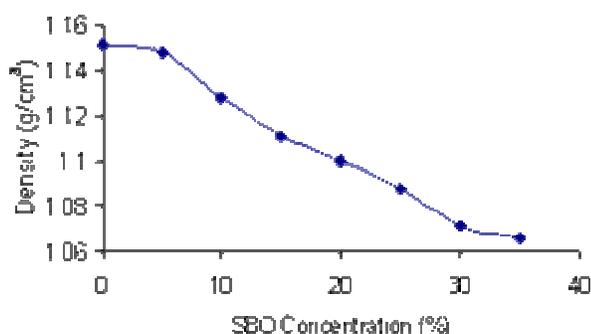


Figure 5. Effect of concentration on the density of methylol urea.

of incidence of the beam of light, the nature of light and the nature of the material (Trezza and Krochta, 2001). Figure 4 presents the effect of SBO on the refractive index of methylol urea resin. Initially, the refractive index increased at 5% SBO inclusion after which a gradual decrease in refractive was observed with increase in SBO concentration until 25% after which the refractive in-

dex began to increase. This result may be due to differences in the level of specific interaction between the two polymers (Qi et al., 2002) resulting in molecular weight, molecular features and molecular orientations (Trezza and Krochta, 2001) depending on morphology and cross-link density.

Density

In the coating industry, the density of a paint binder is important because it influences factors such as pigment dispersion, brushability of paint, flow, leveling and sagging (Lowel, 1990). Figure 5 shows the effect of SBO on the density of methylol urea where the density of the amino resin, decreases gradually with increase in SBO concentration. This trend may be due to differences in the molecular features and morphology which influences the packing nature of resin molecules (Sekaran et al., 2001).

Melting point

The melting point of a polymer has a direct bearing to its thermal property. It is also 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 the brittility. Figure 6 indicates the effect of SBO on the melting point of methylol urea resin. It is observed that the melting point increased initially up to 10% SBO after which a gradual decrease in melting point was recorded. Between 0 – 10% SBO, there are strong specific interactions resulting in the formation of a compact structure thereby introduc-

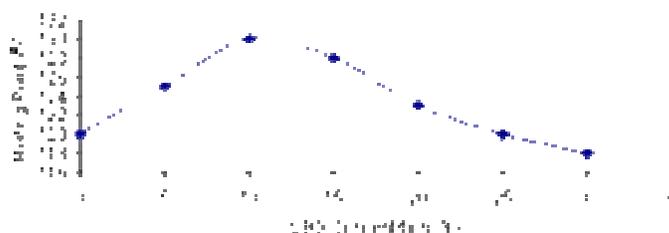


Figure 6. Effect of SBO concentration on the on the melting point of methylol urea.

ing some form of hardness to the system (Qi et al., 2002). After 10% inclusion, the isolated complexes combined leading to the formation of a gel-like intermolecular complex structure which gave rise to an increase in molecular mobility; hence a reduction in melting point (Qi et al., 2002).

Tensile test

One of the shortcomings of urea formaldehyde resin is that it is too hard and brittle to be used as a paint binder (Lowel, 1990). Therefore any attempt to develop a paint binder from this amino resin must overcome this drawback. Table 1 shows the effect of SBO on the tensile strength and elongation at break of methylol urea resin. It is observed that from 0 - 10% blending both the tensile strength and the elongation at break decreased and a gradual increase in these parameters were recorded between 15-25% blending and after this regime, these factors began to decrease again.

Table 1. Effect of SBO on the tensile properties of methylol urea resin.

SBO Concentration (%)	Tensile Strength (kgF/cm ²)	Elongation (%)
0	0.120	140.02
5	0.115	105.11
10	0.075	90.73
15	0.080	110.41
20	0.085	125.00
25	0.121	142.51
30	0.095	125.22
35	0.090	115.31

This non-linear behavior in terms of the mechanical property is caused by the differences in intimate physical interlocking, and the extent of phase separation (Lee and Kim, 2001). This behavior is supported by both viscome-

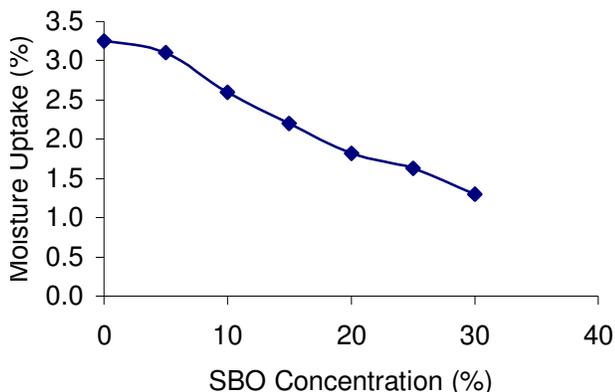


Figure 7. Effect of SBO concentration on the on the moisture uptake of methylol urea.

tric and morphological results. Note that both pure methylol urea resin and its blend with 25% SBO showed the

typical characteristic for ductile polymers: stress whitening followed by necking and drawing (Tai and Li, 2001). The increase in both tensile strength and elongation at break agrees with the works of Wang and co-workers (Wang et al., 2002) on super polyolefin blends.

Moisture uptake

Moisture uptake affects vital properties of polymer materials such as the physical, mechanical, thermal and structural properties. One of the major draw backs of urea formaldehyde resin is poor water resistance (Conner, 1996). In the paint making industry, the moisture uptake of the binder is very crucial because it is responsible for blistering and broominess of paint film (Lowel, 1990).

Figure 7 shows the effect of SBO on the moisture uptake of methylol urea resin. It can be seen that the moisture uptake decreased slightly at the beginning and steeply after 10% blend. The different levels of interactions gave rise to polymers with different morphology and crosslink density (Qi et al., 200). From 0 - 10% blend, the molecular size holes in the polymer structure were more. After this regime, the size of the molecular size holes might have decreased with increase in SBO loading; hence the steep reduction in moisture uptake. The hydrophobic nature of SBO is also responsible for this result.

Dry time

Table 2 shows the effect of SBO on the dry time of blended methylol urea resin at 30°C temperature. The result obtained from this experiment agrees with the report of Yoon and McGrath (2001) on epoxy resins. The relative long period of drying period recorded between 5-10% blending is due to low viscosity (Trumbo et al.,

Table 2. Effect of SBO on the dry time of blended methylol urea resin at 30°C.

SBO Concentration (%)	Dry to touch (h)
0	48
5	72
10	84
15	70
20	60
25	48
30	72
35	Did not dry

2001) which is a consequence of the different level of interaction between methylol urea and SBO at the different blending ratios. The trend from 15 - 25% SBO is due to increase in molecular weight and crosslink density (Tai and Li, 2001). The situation recorded in the 30 and 35%

Table 3. Effect of SBO on the formaldehyde emission of urea formaldehyde resin.

SBO Concentration (%)	Formaldehyde Emission (ppm)
0	0.110
5	0.109
10	0.095
15	0.0817
20	0.0735
25	0.0655
30	0.0650
35	0.0600

Table 4. Comparison of some physical properties of SBO-modified methylol urea films with other paint binders.

Types of Resin	Viscosity (mPa.s)	Refractive Index	Density (g/cm ³)	Melting Point (°C)	Moisture Uptake (%)	Elongation at break (%)	Reference
SBO Modified Methylol Urea	19.39	1.4690	0.85	102	6.5	125	This study
Epoxy-based Divinyl Ester	38.0	ND	1.04	197	ND	ND	Gawdzik and Matynia (2000)
Styrene Modified Epoxy	ND	ND	ND	200	ND		Yoon and McGrath (2001)
Maleic anhydride grafted polypropylene bend with epoxy resin	ND	ND	ND	200	ND	116	Shieh et al. (2001)
Epoxy fumerate Resins	45.0	ND	1.07	110	ND	ND	Gawdzik et al. (2000)
Whey Protein Isolate biopolymer	ND	1.4838	ND	ND	ND	ND	Trezza and Krochta (2001)
Aromatic amines-modified polyethylene	ND	ND	0.96	133	ND		Starostina et al. (2001)
Silicone-Modified styrene-butyl acrylate Copolymer latex	ND	ND	ND	ND	8.6	ND	Wu, et al. (2000)
Rubber Seed oil modified alkyd resins	3.11	ND	0.95	ND	ND		Aigbodion and pilla (2001)
Glycidyl methacrylate and piperazin	ND	ND	ND	ND	ND	1700	Hong et al. (2002)
Epoxy Resins	ND	ND	ND	101	0.04	ND	Hu et al. (2001)
Aqueous Polyurethane	ND	ND	ND	ND	17.2	ND	Lee and Kim (2001)

ND: Not Determined

SBO may be attributed to excess SBO in the blend.

Formaldehyde emission

The emission of formaldehyde during resin cure is one of the drawbacks of urea formaldehyde resins (Kim, 2001). Table 3 shows the effect of SBO on the formaldehyde emission of urea formaldehyde resin. It is observed that the emission level decreased with increase in the percentage of SBO inclusion in the blend. This trend is due to the gradual decrease in the methylol urea content with increase in the SBO content in the blend (Pizzi et al., 2002). The blending process has succeeded in reducing

the emission lower than the permissible level of 0.1 ppm (Pizzi et al., 2002).

Table 4 compares some physical properties of SBO modified methylol urea and that of some convectional paint binders. The table explained that the SBO modified methylol urea is more water resistant, softer and more flexible than some convectional paint binders. This result also suggest that the problems of poor water resistance, hardness and brittility associated with convectional urea formaldehyde (Lowel, 1990) is been addressed through blending of methylol urea resin with SBO. However, the gloss of SBO modified resin is relatively low compared to the literature value.

Conclusion

The interaction between MUR and SBO showed remarkable synergistic properties with 25% of SBO being the optimal inclusion value. The values of moisture uptake, formaldehyde emission, melting point and elongation at break obtained from this experiment are within the acceptable levels required in the coating industry. Further the results of this work indicate that SBO-modified methylol urea is presented as a resin with relatively very low moisture uptake and formaldehyde emission. It also suggests that urea formaldehyde is being softened against the traditional hard and brittle resin. The reduction in density is also a positive value to the coating industry. This type of polymer blend may therefore be recommended as a binder in the coating industry.

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