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Study of a composite from reactive blending of methylol urea resin with natural rubber

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This study was designed to study some physical properties of a composite derivable from reactive blending of methylol urea resin (MUR) with natural rubber (NR). Formaldehyde emission, decreased with increase in NR concentration in the blend. Elongation at break and viscosity recorded an initial increase but gradually decreased with increase in NR concentration. The melting point however showed an opposite behavior. The incorporation of NR significantly lowered both the refractive index and the density of this composite. The highest viscosity was recorded at 50:50% blend ratio. Formaldehyde emission level, moisture uptake and elongation at break recorded for this composite are within acceptable levels required in the coating industry. Also water resistant and flexibility compared favorably with those of conventional paint binders. The low refractive index may be favorable for low gloss coating at low pigmentation levels of coating systems.

Key words: Natural rubber, reactive blending, methylol urea, formaldehyde emission, moisture uptake.

INTRODUCTION

Urea formaldehyde resin cannot be used as a paint binder because of its inherent drawbacks namely brittleness, poor water resistant and formaldehyde emission (Barminas and Osemeahon, 2006a,b). However, blending could be a simple process for developing new composites for coating systems. For example epoxy resins are among the most important high performance thermosetting polymers and have wide use as a structural adhesives and matrix resin for the fibre composites, but their cure resins have one drawback: they are too brittle and have poor resistance to crack propagation (Iijima et al., 2002). The toughness of epoxy resins has been increased by blending them with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN) (Iijima et al., 2002; Ratna et al., 2001).

Song et al. (2000), studied the miscibility and mechanical properties of tetra functional epoxy resin/phenolphthalein poly (ether ketone) blends by dispersing rubbery

particles into the matrix of epoxy resin to enhance its toughness. Nakason et al. (2001), blended maleated natural rubber (NR) with starch and studied both rheological and curing behavior of the reactive blends. Gupta, et al. (2001), modified epoxy resin with high-molecular-weight guayule rubber for coating application.

Miscibility among components has marked influence on the mechanical properties of polymer blends, and hydrogen-bonding interaction in the blends is an important aspect of miscibility (Zhang et al., 2002). Therefore, in a mixture of methylol urea resin and NR in an acidic medium, the NR can undergo cationic polymerization to form an ether linkage between the two different types of polymers. Also, the OH group in MUR could participate in condensation reaction with the methyl group in NR to form a chemical linkage between MUR and NR.

In our previous experiments, we reported the synthesis of methylol urea resin through a new synthetic route termed one step process (OSP) (Barminas and Osemeahon, 2006a, b). The objective of the present work is to obtain a functional composite by blending MUR with NR. The aim is to further reduce formaldehyde emission and moisture uptake of methylol urea resin, while taking the

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advantage of the elastomeric properties of natural rubber molecules to reduce inherent brittleness of the cured methylol urea resin film.

MATERIALS AND METHODS

Materials

Urea, formaldehyde, sodium dihydrogen phosphate, sulphuric acid, sodium hydroxide pellets and sucrose were reagent grades products from BDH. Natural rubber from *Hevea brasiliensis* (NIG805) was obtained as exudates from Rubber Research Institute Benin City, Nigeria. All materials were used as received.

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. Sodium dihydrogen phosphate (0.2 g) was used as a catalyst (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 mixture was then heated in thermostatically controlled water bath at 70°C. The reaction was allowed to proceed for 2 h after which the product obtained was removed and kept at room temperature (30°C).

Preparation of MUR- NR composite films

Blends of MUR and NR were prepared by adding varying amounts of NR (0 – 60%) in MUR resin. The mixtures were stirred and left for 24 h at room temperature (30°C) and then poured into glass petri dishes for casting (Mirmohseni and Hassanzadeh, 2000). The resins were also allowed to cure and set for seven days at 30°C. The physical properties of these films were then investigated.

Determination of physical properties

The viscosity of the polymer blend was obtained from a previous method (Barminas and Osemeahon, 2006a). Other physical properties were determined according to 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 samples was determined by using Hanna microprocessor turbidity meter (Model H193703). The melting point of the different film samples were determined by using Galenkamp melting point apparatus (Model MFB600-010F). The refractive index 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 sample was 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 as reported by Kim (2001). The mold used was made from aluminum foil with a 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 by a refractometric technique using Abbe refractometer. Triplicate samples were used and average value taken.

Tensile test and dry time measurements

Tensile properties (tensile strength and elongation at break) 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 was 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).

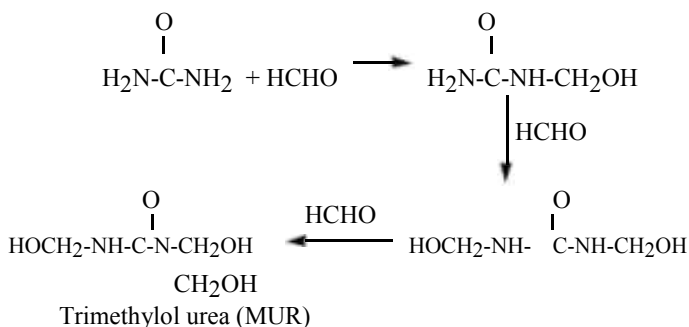
Infrared (IR) spectroscopy

The IR analysis of the dried composite films was carried out by direct scanning of the film using scanning infra-red spectrophotometer (Buck Scientific Inc. Norwalk, CT USA, Model M500) within 600 – 4000 cm⁻¹.

RESULTS AND DISCUSSION

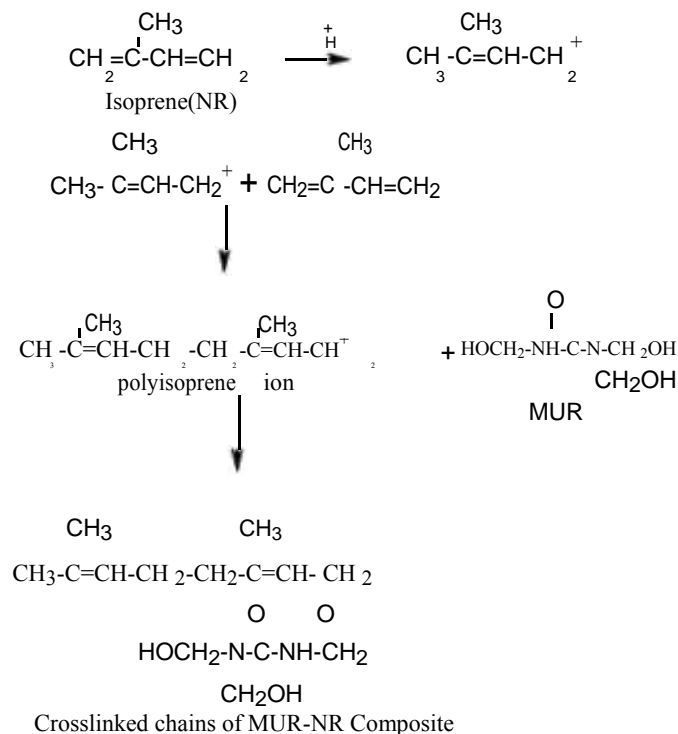
Reactive blending reactions

The reactions that produced trimethylol urea (MUR) involved the addition of formaldehyde to the amine groups of urea as shown by the following reaction scheme:

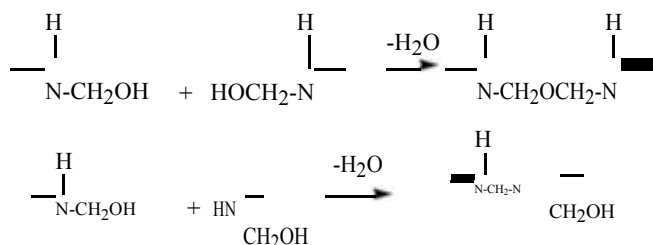


The reactive blending between MUR and natural rubber may be considered in two steps:

- Cationic polymerization of natural rubber in the acidic medium followed by ether linkage onto the MUR chain by polycondensation reaction mechanism to give MUR-NR composite.
- Condensation reactions can still continue to give different polymers thus:

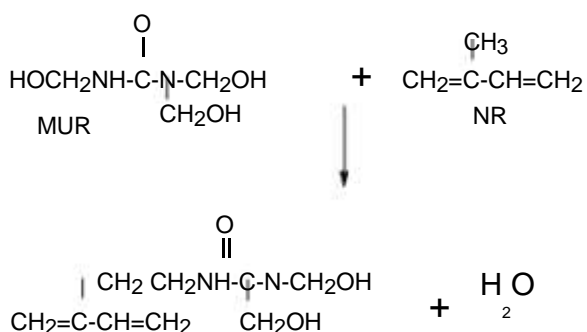


(i) Between two methylol groups or between one methylol group and active hydrogen atoms of the composite as indicated below:



All these reactions may consume methylol groups that might lead to crosslinked composite chains with some level of flexibility, insolubility in water and other solvents.

(ii) Similar reactions may also occur between MUR and the natural rubber.



IR spectra of MUR-NR composite

Figure 1 shows the IR spectra of MUR and the composite. The broad band observed at 3610 cm^{-1} through 1800 cm^{-1} is due to the OH group of MUR. The peaks around 1052 and 1740 cm^{-1} may be due to C-O-C and C=O groups of MUR, respectively (Park et al., 2001). These spectral characteristics were also recorded in the spectra of the MUR-NR composite. The C-O-C in the spectra of the composite indicates the presence of ether linkage such as $-\text{CH}_2-\text{O}-\text{CH}_2-$ which occurred due to crosslinking reaction during polycondensation reactions. New peaks around 887 and 1490 cm^{-1} in the composite represent C=C and $-\text{CH}_2$ scissoring deformation, respectively. Also, the OH peak which appeared at 3601 cm^{-1} in MUR shifted to a higher band (3630 cm^{-1}) in the MUR-NR spectra.

The C=C and $-\text{CH}_2-$ bands in the composite may have originated from the double bonds and the alkyl chains present in NR. The drastic reduction in the OH band in the MUR-NR composite spectra may be ascribed to the consumption of OH groups during the condensation reactions. The band at $\sim 1290 \text{ cm}^{-1}$ may be assigned to $-\text{OH}$ band deformation in $-\text{CH}_2\text{OH}$. The medium band appearing at 1583 cm^{-1} may be ascribed to $-\text{N}-\text{CH}_2-\text{N}$ -groups. The C-H bending mode in $-\text{CH}_2$ or $-\text{CH}_2\text{OH}$ was recorded at 1413 cm^{-1} . These observations may confirm plausible chemical interaction between MUR and NR.

Viscosity

The effect of the concentration on the viscosity of MUR is shown in Figure 2. It indicates an initial drop in viscosity followed by a gradual increase in viscosity with NR content in the blend and drop in viscosity after 50:50% blend ratio. The initial drop in viscosity with NR content is attributable to high extent of interaction of MUR/NR blend (Manchado et al., 2001; Qi, et al., 2002). The drop in viscosity may also be due to a change in morphology or to an interlayer slip (Manchado et al., 2001).

In a dilute system, there are specific interactions and complexes that are isolated from each other with the formation of a compact structure, which reduces the viscosity of the blending solution. However, as the blend concentration rises, the isolated complexes combine and lead to the formation of a gel-like intermolecular complex structure, which leads to the increase of the solution viscosity (Qi, et al., 2002). This explains the trend observed from 20 – 50% NR in the composite. The increase in viscosity may also be due to increase in molecular weight which may be due to reactive blending between MU and NR. The observation from 50% NR above in the blend may be attributed to phase inversion in which the NR formed the continuous phase and the rheological properties tend toward that of the neat NR (Manchado et al., 2001). Hence the incorporation of natural rubber molecules in the formaldehyde resin matrix

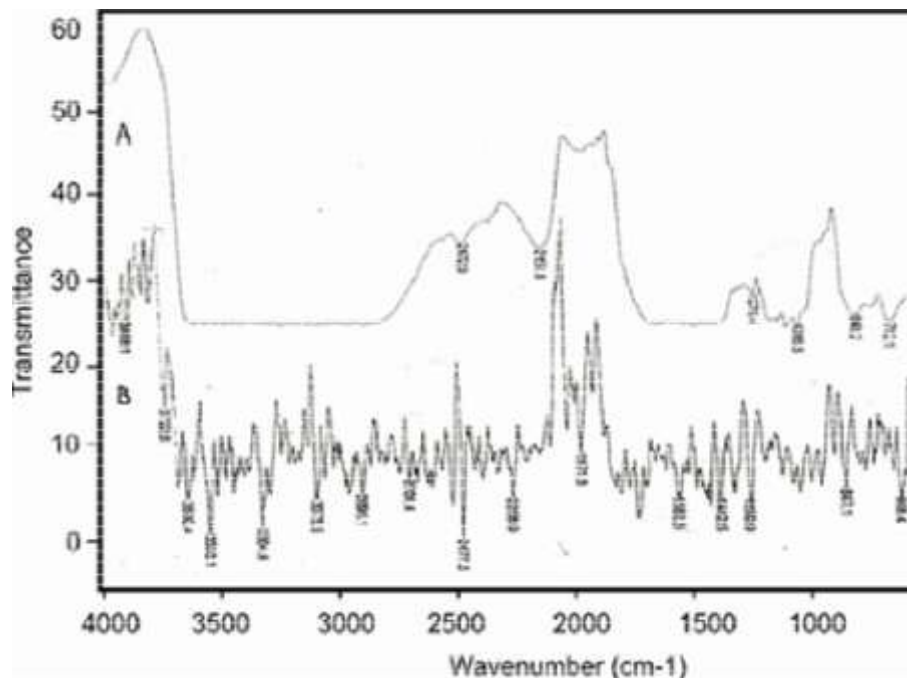


Figure 1. IR spectra of MUR (A) and MUR-NR composite (B).

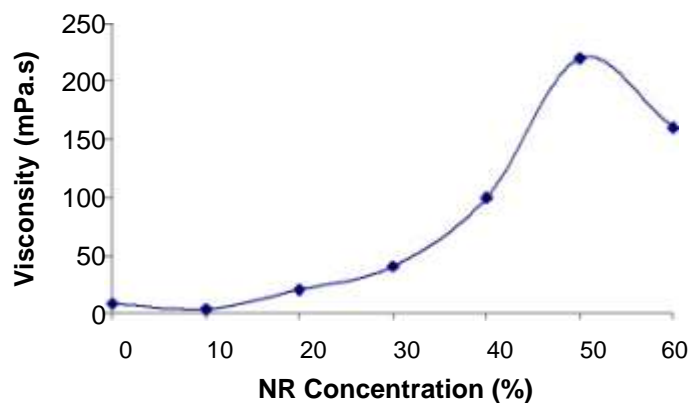


Figure 2. Effect of NR concentration on the viscosity of methylol Urea (formaldehyde/urea mole ratio = 3:1, temperature = 70°C, time = 2 h).

may increase average size and average molecular weight of the composite sample.

Refractive index

Gloss is an important factor of many coating products. The gloss of a paint coating is a function of the refractive index of the surface, the angle of incidence of the beam of light, the nature of light and the nature of the material (Trezza and Krochta, 2001).

The effect of NR concentration on the refractive index of methylol urea resin is shown in Figure 3. It is observed that the refractive index of the blends decrease with increase in NR concentration in the blend. The above result agrees with the report of Gupta et al. (2001) who carried out similar experiment on the blending of epoxy resin with high-molecular weight Guayale rubber for coating applications.

The decrease in refractive index with increase in NR content in the blend is attributable to the microphase separation between the methylol urea resin and the NR (Gupta et al., 2001). Low gloss coating have been traditionally formulated by raising pigment concentration to a point where the roughness induced by the protruding pigment particles causes most of the incident light to be scattered in all direction (Gupta et al., 2001).

However, high pigmentation levels usually have a negative effect on both the mechanical and solvent resistance properties of the coatings. In this context, our novel methylol urea resin/NR blend have a significant role to play as the blend can greatly reduce the gloss of the coating system without any deleterious effect on the mechanical properties or the chemical resistance properties of the coating system. This enables low-gloss coatings to be formulated at lower pigmentation levels.

Density

In the coating industry, the density of the paint binder has a profound influence on factors such pigment dispersion, brushability of paint, flow, leveling and sagging (Lowel,

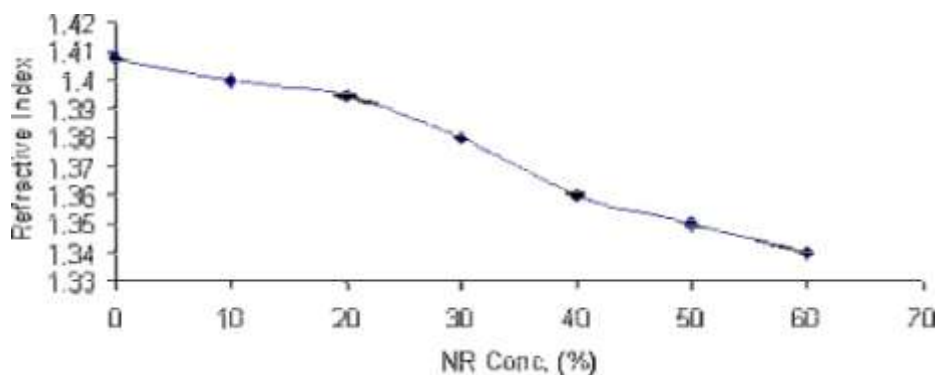


Figure 3. Effect of NR concentration on refractive index of methylol urea (formaldehyde/urea mole ratio = 3:1, temperature = 70°C, time = 2 h).

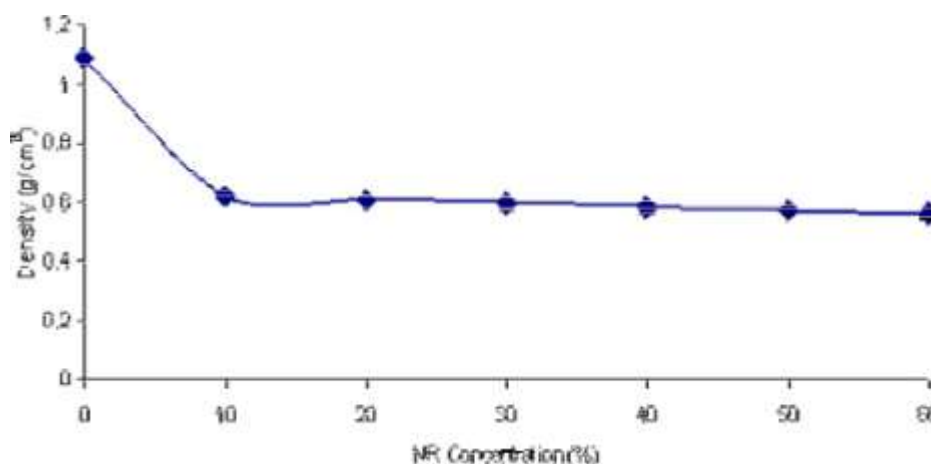


Figure 4. Effect of NR concentration on the density of methylol urea (formaldehyde/urea mole ratio = 3:1, temperature = 70°C, time = 2 h).

1990).

Figure 4 indicates the effect of NR concentration on the density of methylol urea resin. It can be observed that the density dropped sharply from 0 – 10% blending and then marginally decreases from 10 – 60%. The initial sharp drop in the density of the blend at 10% NR content can be explained in terms of high specific interaction at this concentration which lead to a sharp change in morphology of the resin system and hence a sharp drop in density (Manchado et al., 2001; Qi et al., 2002). The gradual reduction in density with increase in NR content in the blend can be ascribed to inefficient molecular chain packing as density depends on free volume and packing efficiency of molecular chain (Chain and Yi, 2001)

Formaldehyde emission

One of the major draw backs of urea formaldehyde resin is the emission of the hazardous formaldehyde during cure (Kim, 2001; El-Naggar et al., 2001; Pizzi et al.,

2001) in the development of paint binder from urea formaldehyde therefore; serious effort must be made to reduce formaldehyde emission to acceptable level.

Figure 5 shows the effect of NR concentration on the formaldehyde emission of methylol urea resin. It can be seen that the formaldehyde emission decreases with increase in NR concentration in the blends. The above result can be attributed to the gradual reduction in the quantity of methylol urea resin in the blend with increase in the concentration of NR in the blend. The result is in consonance with the report of Pizzi et al. (2002) where acetals were used to reduce melamine-urea- formaldehyde content in amino resins adhesive thereby reducing the level of formaldehyde emission.

Melting point

The melting point of a polymer is related to its viscosity, molecular weight and the degree of crosslink density (Markovic et al., 2001; Park et al., 2001). Figure 6 shows the effect of NR concentration on the melting point of me-

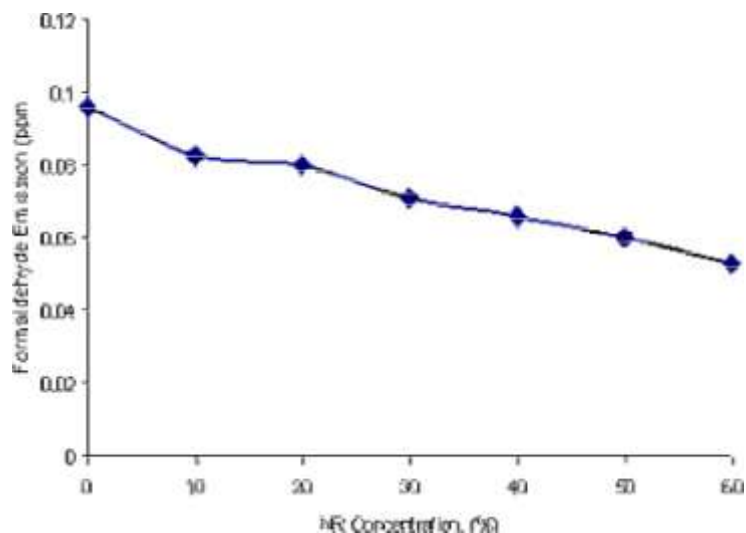


Figure 5. Effect of NR concentration on the formaldehyde emission of methylol urea (formaldehyde/urea mole ratio = 3:1, temperature = 70°C, time = 2 h).

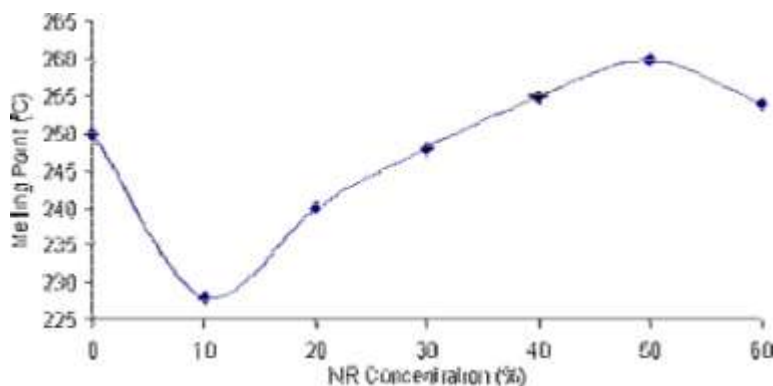


Figure 6. Effect of NR concentration on the melting point of methylol urea (formaldehyde/urea mole ratio = 3:1, temperature = 70°C, time = 2 h).

thylol urea. It is observed that the melting point

Table 1. Effect of concentration of natural rubber on the tensile property of composite.

NR: MUR Ratio	Elongation at break (%)
0:100	140
10:90	620
20:80	470
30:70	400
40:60	370
50:50	340
60:40	405

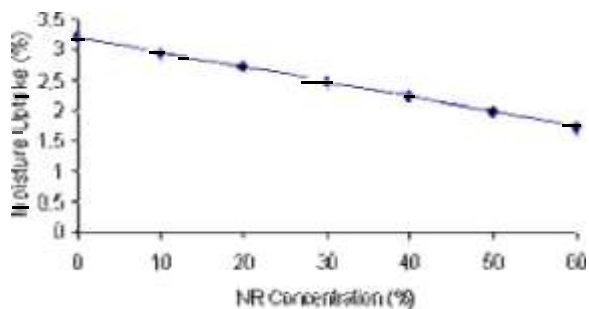


Figure 7. Effect of NR concentration on the moisture uptake of urea (formaldehyde/urea mole ratio = 3:1, temperature = 70°C, time = 2 h).

dropped initially at 10% NR content followed by gradual increase in melting point with increase in NR content. A

Table 2. Comparison of some physical properties of MU/NR film with films from other paint binders.

Types of Resin	Physical Properties						Literature
	Visc (mPas)	RI	Density (g/cm ³)	MP (°C)	MU (%)	EB (%)	
MUR-NR composite(50:50 blend)	220	1.3501	0.5708	260	1.95	340	This study
Epoxy-based divinyl Ester	38.0	ND	1.04	197	ND	ND	Gawdzik and Matynia, 2001
Styrene modified epoxy	ND	ND	ND	200	ND	ND	Yoon and Mc Grath 2001
Maleic anhydride grafted polypropylene bend with epoxy resin	ND	ND	ND	200	ND	11.6	Shieh et al., 2001
Epoxyfumerate resins	45.0	ND	1.07	110	ND	ND	Gawdzik et al., 2002
Whey protein isolate biopolymer	ND	1.4838	ND	ND	ND	ND	Trezza and Krochta, 2001
Styrene-butadiene latex	ND	ND	ND	ND	ND	220	Xie et al., 2001
Aromatic amines-modified polyethylene	ND	ND	0.96	133	ND	ND	Starostina et al., 2001
Silicone-modified styrene-butyl acrylate copolymer latex	ND	ND	ND	ND	8.6	ND	Wu et al., 2000
Aqueous-based polyurethane	ND	ND	ND	ND	25	713	Huang et al., 2000
Rubber seed oil modified alkyd resins	3.11	ND	0.95	ND	ND	ND	Aigbodion et al., 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

maximum was obtained at 50:50 blending followed by a drop at 40:60 methylol urea: NR ratio. The above result can be explained on the basis of differences in molecular weight among the different blends (Markovic et al., 2001; Park, et al., 2001). This is further supported by the viscosity result obtained in this experiment.

In a dilute systems, there are specific interactions and complexes are isolated from each other with the formation of a compact structure, which reduces the viscosity and hence the crosslink density of the blending solution. However, as the blend concentration rises, the isolated complexes combine and lead to the formation of a gel-like intermolecular complex structure, which leads to the increase of the solution viscosity and hence crosslink density (Qi et al., 2002). This explains the trend observed in this experiment.

Moisture uptake

Water uptake affects vital properties of polymer materials such as the physical, mechanical, thermal and structural properties (Hu et al., 2001; Nogueira et al., 2001). One of the major drawbacks of urea formaldehyde resin is poor water resistant (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.

Figure 7 shows the effect of NR concentration on the moisture uptake of methylol urea. It is observed that the moisture uptake decreases with increase in NR content in the blend. This result may be due to the gradual decrease in methylol urea loading with gradual increase in the

NR concentration in the blend. This is so because cured NR is resistant to moisture uptake.

Tensile test

Table 1 shows the effect of NR concentration on the elongation at break of methylol urea resin. The elongation at break had a dramatic increase initially followed by a gradual decrease due to changes in viscosity, molecular weight and crosslinking density of the composite (Wang et al., 2002; Xie et al., 2001). Phase inversion behavior may have occurred after 50:50% blending ratio (Manchado et al., 2001) where the properties of the composite mimic that of pure natural rubber.

Table 2 compares some physical properties of MUR-NR composite with some paint binders. The moisture uptake of the composite is far less than some of the conventional binders implying a potential solution to poor water resistant associated with urea formaldehyde resins. The relatively low refractive may enable low-gloss coatings to paints at lower pigmentation. The low density recorded with NR modification will favor proper adhesion of the binder to the substrate (Gupta et al., 2001). The relatively high melting point of the NR modified resin compared with the available binders signifies good thermal stability even at high level of flexibility indicated by the elongation at break. The viscosity of the composite is high compared with binders named in Table 2.

CONCLUSION

We prepared a composite by reactive blending of a urea formaldehyde resin with rubber and studied some physi-

cal properties that may be exploited for paint formulation. The formaldehyde emission level, moisture uptake, and elongation at break recorded here are within acceptable levels required in the coating industry in terms of environmental safety, water resistant and flexibility of the paint film. The low refractive index of the composite may allow low-gloss coating to be formulated at low pigmentation levels without affecting the tensile or chemical resistance properties of the coating system. Thus, this composite could be considered a potential novel paint binder in the coating industry.

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