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The Use of Epoxidised Natural Rubber Latex for Developing Coloured Adhesives

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Abstract

Adhesives serve many functions in daily life, starting from sticking envelopes to rejoining broken materials. Adhesives are usually developed for a specific purpose and the performances can vary according to their specific end-use. Most of the commercially available adhesives comprised non-renewable or petroleum derived raw materials. Thus, in order to mitigate negative impact of using non-renewable material as the raw material for adhesives, a new type of adhesive containing epoxidised natural rubber (NR) latex is developed. Epoxidised NR latex adhesive was initially prepared and pigment was subsequently added to produce desired colours of the adhesive. Hence, the newly developed adhesive can serve as adhesive and also as paint for art. The adhesives were characterised and the results indicated that they were free from heavy metal contents and volatile organic compounds (VOCs). The adhesives exhibited comparable odour concentration to commercial synthetic-based adhesive. In terms of toxicity level, the adhesive developed exhibited low acute oral toxicity. Peel adhesion test of A4 and drawing papers on stainless steel and glass substrates, opacity and glossiness were also investigated in the present study. This coloured adhesive is deemed to support the STEM (science, technology, engineering and mathematics) learning by indirectly imparting polymer science and technology in art education and further promotes creative learning among school children. The adhesive is also derived from renewable material rendering it more environmentally friendly.

Keywords: epoxidised natural rubber latex, water-based adhesive, water-based paint, dual function adhesive

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Introduction

The aim of the development of coloured adhesives is to increase the use of natural and sustainable material such as natural rubber latex in stationery and artwork. This is in line with the growing awareness of safety and health to use green and environmental friendly materials in crafts and arts.

In the present work, utilisation of epoxidised NR latex in water-based adhesive formulation with subsequent incorporation of pigments imparts additional function of adhesive as a medium for art or paint. Twelve colours of adhesive were successfully prepared and was shown to be suitable for use in art and craft activities such as collage making, painting and gluing paper, polystyrene, sheet of foam and many other materials. Owing to the stringent environmental and safety regulations worldwide, the coloured adhesives were tested for heavy metals content, volatile organic compounds (VOCs), odour concentration and acute oral toxicity. The peel adhesion of A4 and drawing papers on stainless steel and glass substrates were measured. In addition to the use for gluing, the coloured adhesives containing

epoxidised NR latex were also used as a medium for art or paint, hence the opacity and glossiness were also examined and further compared with the commercially available poster colours.

Literature review

Adhesives and the applications of adhesives are ubiquitous. In general, adhesives are either produced from natural or synthetic sources, but mostly are synthetically produced from petroleum-derived feedstock which are depleting, non-renewable and susceptible to fluctuation in price. Historically, a large portion of the adhesives in the market was produced using solvents, with NR being a particularly preferred material. It was first used in medical adhesives tapes and plasters in 1845 containing a mixture of India rubber, turpentine extracts, Peruvian balsam and pine gum (Butler, 1989). In hindsight, epoxidised NR has also been researched in adhesive applications. Epoxidised NR is a type of modified rubber where a portion of the –C=C– of the NR is chemically converted to epoxide groups useful for bonding substrates with different polarity and it has been evaluated as footwear adhesive (Maarof, 1998) and a cover adhesive to bond variety of vulcanisable and vulcanised rubbers to metals (Loo, 1989). Imran and Poh (2011) have also conducted systematic studies on epoxidised NR in pressure-sensitive adhesive applications.

Increasing environmental concerns and regulations to reduce the VOC emissions have driven adhesive manufacturers to shift towards water-based technology. As a water-based adhesive, NR latex has been widely used in applications that include self-sealing paper envelopes, leather adhesives, tile adhesives and anchor coat for tufted carpets (Gazeley, 1981). Adhesive comprising epoxidised NR latex has also been explored in pressure-sensitive adhesive applications (Wong & Chen, 1988; Bakar et al., 2014) and wood adhesives (Thongnuanchan et al. 2007; Bakar, 2009).

Methods

Materials

The water-based adhesive containing epoxidised NR latex (Ekoprena®-25, 25% mole of epoxidation) and cellulose derivative was first prepared using an in-house proprietary formulation (Bakar et al., 2018). The adhesive was further mixed with pigment using dispersion blade mixer at 200 rpm for 30 minutes to obtain the desired colours. Twelve coloured adhesives were prepared namely white, red, blue, yellow, green, black, orange, dark brown, lime green, sky blue, pink and purple.

Methods and properties of coloured adhesives

Heavy metals content and volatile organic compounds (VOCs)

Heavy metals content and VOCs in the coloured adhesives were tested to comply with Eco-labelling Criteria for Adhesives (Malaysian Standard, 2012). This Malaysian Standard establishes the criteria in order to reduce the use of hazardous and polluting substances as well as restriction on highly toxic materials in adhesives. The heavy metal elements in the coloured adhesives were determined using test methods as listed in Table 1, whilst VOCs below 200 °C boiling point in the adhesives were determined referring to USEPA SW – 846 Method 8260B.

Table 1 Determination of elements in coloured adhesive

Elements	Test method
Lead (Pb)	EPA Method 3050B; EPA Method 3052; EPA Method 6010B (1996, Rev.2)
Mercury (Hg)	USEPA 7471A (1994, Rev.1)
Hexavalent chromium (Cr6+)	EPA 3060 (1996)
Polybrominated biphenyls (PBB)	USEPA 3540C, USEPA 8270C (2004)
Polybrominated diphenyls ethers (PBDE)	USEPA 3540C, USEPA 8270C (2004)
Cadmium (Cd)	BS EN 1122:2001

Acute oral toxicity

The acute oral toxicity of coloured adhesive was evaluated in Sprague-Dawley rats. This study was performed in compliance with the appropriate provision of the Organisation for Economic Cooperation and Development (OECD) 2002, Test No. 423: Acute Oral Toxicity – Acute Toxic Class Method, OECD Guidelines for Testing of Chemicals, Section 4, OECD Publishing, Paris.

Odour concentration

One gram of coloured adhesive was weighed directly into a nalophan bag and then was immediately purged with 3 L nitrogen gas. Further analysis was carried out using DynaScent Digital Dynamic Olfactometer referring to MS 1963: Air Quality – Determination of odour concentration by dynamic olfactometry.

Peel adhesion

A 1 x 7 inch strip of the paper was cut and then approximately 50 µm wet film of coloured adhesive was coated on the paper (drawing and A4 papers) using an automatic film applicator (TQC Sheen Model SH1133N). A strip of adhesive paper was bonded to substrate (stainless steel and glass) by rolling the paper on to the surface with a weight of 2.05 kgf. The peel adhesion at 180^{o} angle was measured at 300 mm/min peel rate using Universal Testing Machine (Instron, Model 5564). The average of peel adhesion was taken from five replicates.

Opacity

The opacity or hiding power of coloured adhesive was measured using Opacity Reflectometer (Sheen-Opac SH310). It measures the diffusely reflected light from the test surface. The coloured adhesive was applied or coated onto black and white card and air dried. Reading was taken on the coating over the black portion followed by a reading taken over the white portion. The contrast ratio or hiding power was calculated as follows:

$$Hiding\ power\ (\%) = \frac{Black\ reading}{White\ reading} \times 100$$

Glossiness

Coloured adhesive was coated on A4 paper and air dried at room temperature. Then, the glossiness of the coloured adhesive was measured using BGD 516/1 Intelligent Glossmeter (60˚).

Results and Discussion

Heavy metals content, VOCs and odour concentration

Concerns regarding the environment as well as the health and safety pertaining to the users or consumers adhesives products are gaining momentum worldwide. Thus, Malaysian Standard: Eco-labelling criteria for adhesives (MS 2498:2012) have been referred to obtain good environmental performance benchmarks for adhesives. Two major hazardous substances requirements are outlined, namely limits of heavy metals content and level of VOCs. Several workers (Guo et al., 2000 and Kim et al., 2006) reported that odour emanated from the adhesive were due to the VOCs in the adhesive which can cause adverse health impacts on consumers.

Table 2 shows heavy metals content of lead (Pb), mercury (Hg), hexavalent chromium (Cr^{6+}) and cadmium (Cd) are below than 2 ppm whilst polybrominated biphenyls (PBB) and polybrominated diphenyls ethers (PBDE) are below than 5 ppm. The restricted limits for all elements are 1,000 ppm as stated in the Malaysian Standard. Furthermore, the VOCs including monocyclic aromatics, oxygenated compounds, fumigants, halogenated aliphatics, halogenated aromatics and trihalomethanes in the coloured adhesives containing epoxidised NR latex were below the detection limit of reporting at 0.5 mg/kg (0.00005 % by weight). In addition, the VOC values obtained were far below than 5 % by weight referring to levels of VOCs requirement in the MS 2498: 2012. However, the coloured black adhesive released comparable odour emission with only 3 % higher in odour concentration value than commercial synthetic-based adhesive as shown in Table 3.

Table 2 Heavy metal contents of coloured adhesives

Elements	Coloured black adhesive (ppm)	Coloured sky blue adhesive (ppm)
Lead (Pb)	ND < 2	ND < 2
Mercury (Hg)	ND < 2	ND < 2
Hexavalent chromium (Cr^{6+})	ND < 2	ND < 2
Polybrominated biphenyls (PBB)	ND < 5	ND < 5
Polybrominated diphenyls ethers (PBDE)	ND < 5	ND < 5
Cadmium (Cd)	ND < 2	ND < 2

*ND = Not detected

Table 3 Odour concentration of coloured adhesive and commercial synthetic based adhesive

Sample	Odour concentration (ou/m^3)
Coloured black adhesive	3,326
Commercial adhesive	3,217

Acute oral toxicity study

Acute oral toxicity in rodents was studied to assess the toxic potential of chemicals and health hazards that expected to arise from a short-term exposure by the oral route. The route of administration in animals was by oral gastric intubation, wherein being representative route of exposure in human. This study could provide initial information on the mode of toxic reactions of coloured adhesives and subsequently serves as a basis for classification and labelling. During the study period, there was no evidence of clinical or toxic manifestation, in which the animals did not showed any weight loss. Also, all animals showed no gross lesion of the brain, kidneys, lungs, liver, stomach, spleen, heart and pancreas during necropsy. The coloured adhesive containing epoxidised NR latex did not demonstrated any adverse toxic reaction at 2000 mg/kg body weight on all the animals used. The acute oral toxicity of the adhesive is considered as Category 5 or Unclassified according to OECD Guideline 423 (2002).

Peel adhesion

Peel adhesion test was performed to measure the ability of the adhesive to resist its removal upon peeling. Table 4 shows peel adhesion of coloured adhesives using A4 and drawing papers as a backing, and tested on stainless steel and glass substrates. The peel adhesion of coloured adhesives using drawing paper are in the range of 7 to 8 N/25 mm on stainless steel whilst 3 to 4 N/25 mm on glass substrates. On the other hand, the peel adhesion using A4 paper are in the range of 3 to 5 N/25 mm on stainless steel whereas on glass are in the range of 2 to 3 N/25mm. In comparison to commercial adhesive, the peel adhesion of commercial adhesive is lower than coloured adhesives for both types of papers.

Table 4 Peel adhesion of coloured adhesives

Sample (N/25mm)	A4 paper		Drawing paper	
	stainless steel	glass	stainless steel	glass
Coloured adhesive black	4.73±0.13	2.82±0.27	7.29±0.87	3.34±0.35
Coloured adhesive sky blue	3.29±0.29	2.04±0.22	7.45±0.59	3.63±0.27
Commercial adhesive	0.17±0.01	0.27±0.02	4.17±0.13	3.50±0.20

Opacity and glossiness

Opacity and glossiness are among the optical properties for paint. In developing paint, pigments are used to impart colour, opacity or other special characteristics to modify the optical properties of paint (Alua, 2012). Opacity or hiding power refers to paint's capacity to completely obliterate the colour or different colours of a substrate. The greater the opacity, the less coating is required to obtain adequate hiding. Table 5 shows the hiding strength of coloured adhesive and commercial poster colours. The results suggested that the hiding power or contrast ratios of commercial poster colours were in the range of 78 and 100 %, indicating good opacity in one coat. However, coloured adhesives, namely yellow, green, lime green, red, orange and blue showed poor hiding power, where 3 to 4 coats may be needed to obtain

the same effect. In relation to the properties of paint, this occurrence could be largely due to low pigment volume used in the formulation. If necessary, this drawback can be overcome by adding pigment extenders in the formulation.

Table 5 Hiding power of coloured adhesives

Samples	Coloured Adhesive	Commercial Poster Colour
Yellow	15	78
Green	11	100
White	71	92
Lime green	52	98
Red	13	86
Orange	29	91
Blue	10	99
Dark Brown	100	99
Purple	88	100
Pink	90	90
Black	100	100
Skyblue	96	99

Paint glossiness is measured using instrument readings of reflectivity taken at different angles from vertical. Paints aesthetic properties can be described as flat, eggshell, satin, semi-gloss and gloss finishes as shown in Table 6. The coloured adhesives containing epoxidised NR latex were glossier than commercial poster colours as shown in Table 7. This coloured adhesive can be classified as eggshell with gloss values between 5 and 12 whilst commercial poster colours showed flat paint with gloss value less than 5.

Table 6 Paint Classification and Gloss Value (MPI Architectural Standards, 2019)

Type of Paint Finishes	60˚ Gloss
Flat	<5
Eggshell	5 – 20
Satin	15 – 35
Semigloss	30 – 65
Gloss	>65

Table 7 Measurement of gloss value using a 60° gloss meter

Colour	Coloured Adhesive (Batch 3)	Commercial Poster Colour
Yellow	11.1	1.6
Green	7.6	0.7
White	8.4	2.0

Lime Green	10.1	1.1
Red	9.0	0.8
Orange	10.4	1.0
Blue	8.2	0.6
Dark Brown	7.8	0.8
Purple	5.9	0.8
Pink	6.8	2.0
Black	10.1	0.4
Skyblue	5.4	1.0

Conclusion

The coloured adhesives with additional function as paint consists of naturally occurring, renewable and green materials such as epoxidised NR latex impart a more environmentally friendly characteristic for stationery uses and artwork. The Malaysian Standard: Eco-labelling criteria for adhesives (MS 2498:2012) was referred to define the hazardous substances in coloured adhesive, namely heavy metals content and VOCs. The coloured adhesive was found to comply with the Malaysian Standard, where no heavy metals and VOCs were detected. Exhibiting low odour concentration and low acute oral toxicity render the coloured adhesive suitable to be used by school children as well as professional artists. Furthermore, the peel adhesion of drawing and A4 papers were higher compared to commercial synthetic-based adhesive. In terms of paint properties, the coloured adhesives were glossier than commercial poster colours, although some of the colours showed poor hiding power. In conclusion, this coloured adhesive can be regarded as a greener alternative for conventional adhesives and also functions as colouring materials as a substitute for poster colours and acrylic colouring materials.

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