Metallurgy and materials
Metalurgia e materiais

Lignin-modified road marking paint: weathering aging studies

Amanda Petronilha Pereira[1,5]
https://orcid.org/0000-0003-2896-1383
Júlia Lopes Ribeiro[2,6]
https://orcid.org/0000-0001-9991-7596
Ana Carolina Ferreira Oliveira[2,7]
https://orcid.org/0000-0003-0418-505X
Claudia Karina Barbosa Vasconcelos[2,8]
https://orcid.org/0000-0002-8675-2996
Marcelo Machado Viana[3,9]
https://orcid.org/0000-0002-6682-2504
Vanessa de Freitas Cunha Lins[4,10]
https://orcid.org/0000-0002-6357-9553

[1]Universidade Federal de Minas Gerais – UFMG,
Departamento de Engenharia Mecânica,
Belo Horizonte – Minas Gerais – Brasil.

[2]Pontifícia Universidade Católica de Minas Gerais
– PUC Minas, Departamento de Física e Química,
Departamento de Engenharia Química,
Belo Horizonte – Minas Gerais - Brasil.

[3]Universidade Federal de Minas Gerais - UFMG,
Departamento de Química,
Belo Horizonte – Minas Gerais - Brasil.

[4]Universidade Federal de Minas Gerais - UFMG,
Departamento de Engenharia Química,
Belo Horizonte – Minas Gerais - Brasil.

E-mails: [5]amanda.pereira@kroton.com.br,
[6]juubss.lops@gmail.com,
[7]carolinaferreira5708@gmail.com,
[8]claudia@gaiahresearch.com,
[9]marcelo@gaiahresearch.com, [10]vlins@deq.ufmg.br

Abstract

The accelerated artificial aging with ultraviolet radiation, viscosity, density, no-pick-up time, flexibility, and abrasion resistance of lignin-modified road marking paint were evaluated. The addition of lignin did not cause significant changes in the physical chemistry, flexibility and no-pick-time test compared to the precursor paint. The addition of 1.00 wt. % of lignin increased the abrasion resistance by 36%. The Fourier Transform Infrared technique performed before and after exposure to Weather-o-meter aging chamber has shown the cleavage of ester groups that are present in acrylic-based resin. The incorporation of 0.10 wt.%, 0.25 wt.%, and 1.00 wt.% increased the photodegradation resistance of the road marking paint inhibiting the ester group and side-chain scissions, since the C-O and C=O band intensity increased after irradiation. The introduction of lignin delayed the yellowing of the aged samples and improved mechanical and photophysical properties besides being a good strategy for the biomass waste utilization of the paper industry.

Keywords: road marking paint, lignin, acrylic resin, photodegradation, weathering aging.

1. Introduction

As reported by the National Transportation Confederation (CNT) Yearbook of 2018 (CNT, 2020), the federal paved road network in 2017 in Brazil was 213,452.81 km. For the year 2018, an additional of 44,280.9 km were paved (CNT, 2020). The CNT report also indicates that horizontal and vertical signage was the most deteriorating aspect among paved federal and state highways, with 59.2% of the over 105,000 km evaluated showing problems with lane paintings, lateral and central (CNT, 2020). The road marking paint was nonexistent in 21.4% of the sections that were evaluated (CNT, 2020). Poor horizontal signaling increases the risk of accidents.

The four major binder-based marking systems assessed were solvent-borne paint; water-based (WB) paint; thermoplastic and thermo spray plastic; methyl methacrylate cold plastic and methyl methacrylate cold spray plastic, also referred to as methyl methacrylate (Mirabedini *et al.*, 2020; Hadizadeh *et al.*, 2020; Cruz *et al.*, 2016). Water-based road-marking (WBRM) paints are environmentally friendly due to their water-based resin composition and low level of volatile organic compounds (VOC) (Fatemi *et al.*, 2006; Burghardt and Pashkevich, 2018). The emissions of VOC reach approximately 25% for solvent-borne paints and below 5% for water-borne paints (Pashkevich *et al.*, 2020). The water-based road marking paints have a higher resistance against fire risk, a well dust protection, and a better hygienic conditions during production and application (Fatemi *et al.*, 2006). The acrylic emulsion resins are the basic components of water-based paints.

Research concerning roadway marking visibility, a relevant property of road paints, has grown since the beginning of the 20th century (Nance and Sparks, 2020). Improvements in roadway marking visibility have included streetlight design, alternative glass beads, LED markers, fluorescent materials, and now, phosphorescent materials (Nance and Sparks, 2020). The life cycle assessment results, considering the whole life cycle from manufacturing to disposal, showed that a global warming potential reduction of more than 50% can be achieved by a more durable road marking system (Cruz *et al.*, 2016). The service life and photodegradation resistance of RM paint can be improved by using lignin addition.

According to Chen and Wan (2017), lignin is a biopolymer and a sub-product of cellulose/paper industry. Aro and Fatehi (2017) reported a 50-70 million of tons of lignin production annually. It is so far the largest biopolymer available. Hence, studies have been carried out to find applications for lignin in the market for several areas such as medicine, pharmaceutical industry, and refractory industries. As commented by Bajwa *et al.* (2019), despite the growing number of possibilities of converting lignin into commercial materials and/or fuel, now-a-days, the largest majority of the produced lignin from the paper industry is burned as low value fuel to generate electricity and heat. Some research initiatives are worth mentioning. The study done by Batista *et al.* (2018) showed positive results for the use of the biopolymer lignin in the asphalt binders modified. The insertion of lignin as the modifying agent has shown efficient for the lifetime increase and the asphalt behavior, mostly because of the thermal resistance raise, as well as the photo-degradation resistance as a result of the lignin's antioxidant property. The research done by Brewer (2011) showed that the presence of the phenol groups existing in its structure ensures antioxidant properties, since hydroxyl groups from the phenolic group act as electron donor groups, neutralizing a free radical formed during the photo-oxidation.

This research aims to study the effects of the lignin addition on photodegradation of RM paints. Physical-chemistry properties, no-pick-time, abrasion, viscosity, density, and flexibility of water-based lignin-modified road marking paints were also evaluated. The study has an innovative character since the literature on it is scarce and has relevance for contributing to the reduction of solid waste generated by the pulp and paper industries, increasing the durability of road marking paints and contributing to the development of a new material: lignin-modified road marking paint.

2. Materials and methods

The alkaline lignin/Kraft lignin was acquired from Sigma Aldrich. A commercial white RM paint based on acrylic resin emulsified in water was used. The RM paint contains acrylic resin (31.80 wt.%), dolomite (50.47 wt.%), titanium (rutile – 10.40 wt.%), and minor contents of antifoam, dispersant, ammonia, sequestrant, and thickener. The lignin used was soluble in water, its molar mass is 10000 g.mol-1, and the Kraft lignin has 4 wt.% of sulfur, and pH 10.5 (concentration of 3 wt.%).

The lignin concentrations selected for this study were 0.10, 0.25 and 1.00 (wt.%) lignin in relation to the mass of the paint. Mixing was performed using "Cowles" disperser at a speed of 800 rpm for 15 min. The Kraft lignin was post-added to the finished paint.

2.1 Characterization

ATR-FTIR analysis (Attenuated Total Reflectance - Fourier Transformed Infrared Spectroscopy) was performed to identify the functional groups in lignin. The FTIR spectrum was obtained by using a Bruker equipment, Alpha model, using the ATR method. The spectrum was obtained in the region between 3800 to 400 cm-1 with 32 accumulations and resolution of 4 cm-1.

After the addition of lignin to the RM paint, quantitative and qualitative properties of the paint were evaluated, and their results were compared with the requirements of the NBR 13699 Brazilian Standard. All experiments were performed in triplicate. Viscosity was determined using the Stormer viscometer according to the ASTM D562-10 (2014) standard. Three different masses were selected to determine the time, in seconds, required for 100 rotor revolutions, in the range from 27 s to 33 s. The consistency, in Krebs units (KU), was obtained using the equipment. Considering the International

System of Units (SI), the Krebs unit corresponds to the mass (g) that flowed in a given time. Density of the samples was determined using a metal pycnometer with an approximate capacity of 100 cm³, according to the ASTM D1475-98 standard. Density is the difference in mass of the pycnometer with and without a sample, divided by the volume of the pycnometer. The flexibility test was performed according to the ASTM D522-93a (2008) standard using the Ericksen Instruments conical mandrel. The paint was applied to metal plates and, after 24 h, the plates were placed in the oven at a temperature of $50 \pm 5°C$, for 2 h. After the plates reached room temperature, they were folded around the metal cylinder at an angle of 180°. The painted aluminum panels were visually analyzed in the deformed region in order to verify the loss of adhesion, cracks, and other changes in the paints.

The drying time test in the pick-up time is one of the requirements contained in the ABNT NBR 15438 (2006) standard for horizontal road signaling. This consists of allowing a steel cylinder with rubber rings to roll freely over the painted glass plate. The drying time in the pick-up time, in minutes, corresponds to the time between painting the plate and the time when the paint is no longer adhered to the rubber rings of the cylinder. The maximum time allowed is 12 minutes.

The abrasion resistance analysis was carried out using glass plates, with dimensions of 150 mm x 200 mm x 3 mm and a 0.6 mm extender for applying the paint. The abrasive used was aluminum oxide (Al_2O_3), 99% pure, electro fused, grain 24, and density of 3.95 ± 0.02 g.cm⁻³. The test was carried out according to the ABNT 15438 (2006) Brazilian standard. Five measurements of the painted plate thickness were made, according to the ABNT NBR 10443 standard, and the average thickness was calculated. The sample was fixed on the abrasimeter so that the abrasive jet hit the plate. A volume of 4000 mL flowed through the abrasimeter repeatedly until an elliptical area with a diameter of approximately 4 mm appeared on the surface of the plate. The volume of abrasives required to perform the test is equal to a factor 0.300 multiplied by the total volume of abrasives (L) divided by the average thickness of the paint film (mm). The average thickness of the paint film was 5 mm.

2.2 Color change

Differences in the tonality of the samples were measured using a spectrophotometer by reflectance, DataColor 650® model (d/8° measurement geometry, light source xenon lamp, illuminant D65, observation angle of 10° and CIELAB system).

The CIELAB parameters L, a, b (Commission International de l'Eclairage) and E were measured at 5 points of the samples and the mean value was obtained. The axis L represents the luminosity which varies from 100 (white) to 0 (black), a and b represent the chromatic coordinates (+a is for red, -a for green, +b for yellow and -b for blue). Values of L, a and b were used to calculate the overall color variation, ΔE, according to the equation (1):

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

(1)

Where, Δ L = L difference before and after aging, Δa= a difference before and after aging, Δb= b difference before and after aging.

2.3 Accelerated aging resistance test

There are three wavelength intervals: UV-C (100-280 nm), UV-B (280-315 nm), and UV-A (315-400 nm) in the UV spectrum 13. Ozone drastically reduces the penetration of radiation with wavelengths shorter than 320 nm and completely excludes those below 290 nm, then only UV-B and UV-A reach the Earth's surface. About 5% of the total energy of the UV spectrum that reaches the Earth's surface is UV-B radiation , and UV-A is responsible for the remaining 95 %. The Weather-Ometer Enclosed Arc Lamp Chamber reproduces the spectrum of solar radiation in the ultraviolet (UV) visible, and infrared (IR), from 340 nm to 800 nm using xenon arc lamps; thus it provides the best correlation to natural outdoor exposures for most applications.

The artificial aging test was performed in a Weather-Ometer Enclosed Arc Lamp Chamber, Atlas CI4000 model. Aluminum panels were painted with 0.25 mm thickness and exposed to radiation with 8 xenon arc light sources, with irradiation intensity of 0.35 ± 0.02 W.m⁻². The samples were exposed for 400 h in alternating cycles of: 102 minutes of light, followed by 18 minutes of light and moisture (spray), at a temperature of 63 ± 5 °C, according to the ASTM G 155 Standard. The samples of road marking paint were arranged in the lateral walls of the weathering chamber and the xenon lamp was in the middle of the chamber.

The aged samples were analyzed by using the FTIR technique in the Bruker apparatus, Alpha model, by the ATR (Attenuated Total Reflectance) method under a nitrogen atmosphere. The spectrum was obtained in units of absorbance between 4000 - 400 cm⁻¹ with 32 accumulations and resolution of 4 cm⁻¹. The normalization procedure was performed by using the ORIGIN software to calculate the areas of the bands.

3. Results

The FTIR spectra of lignin and road paint are shown in Figure 1. The FTIR spectrum of lignin (Fig. 1a) showed the O-H functional group at 3366 cm⁻¹ indicating water absorption, and a strong broad C-H stretching at the 2934 cm⁻¹. In the 1900 and 900 cm⁻¹ regions, several absorption bands are noticed due to the functional groups constituent of the lignin as shown in Table 1. The bands at 1584 and 1505 cm⁻¹ related to aromatics demonstrated that lignin has a potential as an antioxidant. Balasundram *et al.* (2006) attributed a higher oxidant activity of lignin to the phenolic hydroxyl groups in aromat-

ics. Groups associated to guayacyl and syringyl were identified at the 1262 cm^{-1} to 1035 cm^{-1} range. Pandey (2005) showed the infrared spectra of Klason lignin isolated from softwood (Pinus roxburghii), and the reported spectrum agrees with that obtained in this study. Figure 1(b) shows a FTIR spectrum of RM paint which typical bands are described in Table 2.
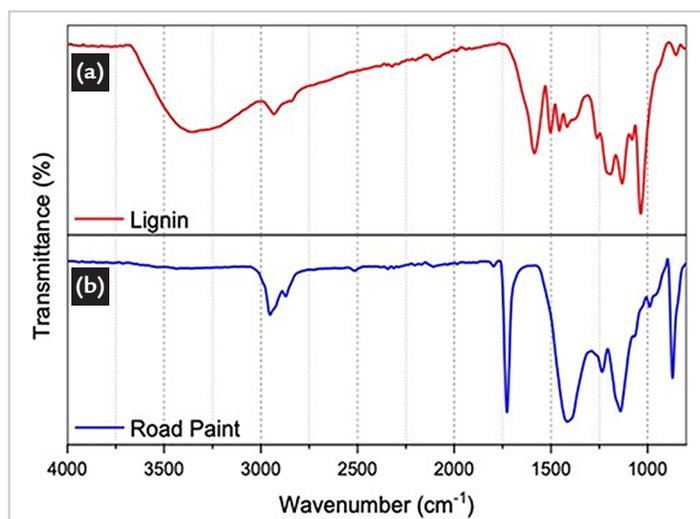

Figure 1- FTIR spectra of (a) lignin and (b) dried road marking paint.

Table 1 - FTIR bands observed in lignin.

Infrared frequency (cm^{-1})	Assignment
3366	O-H stretching
2934	C-H stretching
2846	C-H stretching
1584	Aromatic skeletal vibration + C=O stretching
1505	Aromatic skeletal vibration
1458	C-H deformation (methyl and methylene)
1417	C-H in-planed formation with aromatic ring stretching
1262	C-O of guaiacyl ring
1207	C-O of guaiacyl ring
1131	Guaiacyl C-H and syringyl C-H
1082	C-O of secondary alcohols
1035	C-O of primary alcohol, guaiacyl C-H
854	C-H out-of-plane

Table 2 - Main bands analyzed in the FTIR spectra of road paint.

IR frequency region (cm^{-1})	Functional groups and vibrational modes
2800–3000	C–H stretching: all the samples before and after aging presented two bands at 2870 and 2952 cm^{-1}
1700–1750	C=O stretching: in all spectra, the carbonyl stretching absorption occurs at 1731 cm^{-1}
1300–1500	C–H bending (CH$_2$): bands at 1450 cm^{-1} and 1385 cm^{-1} were ascribed to C-H asymmetric and symmetric deformation vibration of CH$_2$ and CH$_3$
900–1250	C–O stretching and C–C skeletal vibrations: In this frequency region, the samples showed the most intense one at approximately 1150 cm^{-1} and other two bands evidenced at 997 and 1245 cm^{-1}. Literature reported the stretching of the ether from the ester group at 1143 cm^{-1}
870	Asymmetric CO$_3$ deformation to dolomite

3.1 Characterization of modified paint

Table 3 shows the average viscosity, density, drying time, and volume of abrasives of paint samples. A systematic increase of the paint density as the amount of lignin added increases was verified. After the addition of 1.00 wt.%, the viscosity increased 3.40% compared to the original paint. However, all viscosity results are in accordance with the ASTM D-562 standard. These properties ensure that lignin-modified road marking paint is sufficiently fluid for pumping during application and plant operations.

Table 3 - Properties for paint samples studied.

% wt. Lignin	0.00	0.10	0.25	1.00
Viscosity (KU or g)	89.3±0.50 (11.5 g)	90.0±0.8 (11.5 g)	90.3±0.5 (11.6 g)	91.7±1.2 (11.8 g)
Density (g/cm³)	1.71±0.02	1.74±0.03	1.78±0.01	1.79±0.01
Drying time (min)	12.0 ± 0.2	12.0 ± 0.4	12.0 ± 0.1	12.0 ± 0.2
Volume of abrasive (L)	73.91±1.48	80.81±2.68	77.70±3.75	100.73±1.62

Standard acrylic demarcation paint samples containing 0.10%, 0.25% and 1.00% of lignin had the same average drying time value (12 minutes). This time was sufficient for painting the plate and performing the test, since the paint was not adhered to the steel cylinder rubbers, as can be seen in Figure 2. In this study, the amount of lignin added to paint was small and did not influence the drying time.
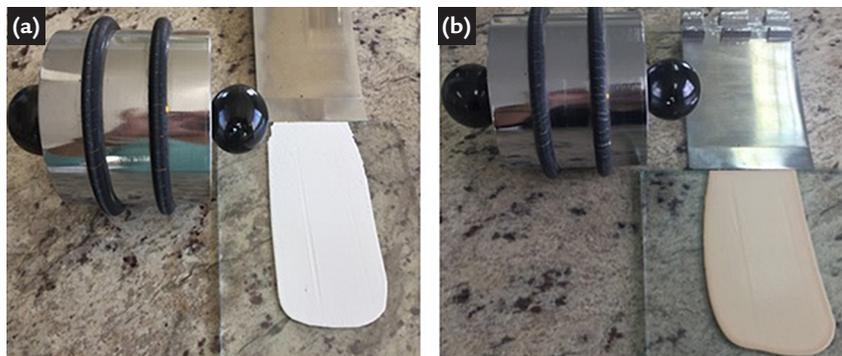

Figure 2 - Images of the no-pick-up time test for samples (a) without lignin and (b) containing 1.00 wt. %.

Standard acrylic demarcation paint samples containing 0.10%, 0.25% and 1.00% of lignin had the same average drying time value (12 minutes). This time was sufficient for painting the plate and performing the test, since the paint was not adhered to the steel cylinder rubbers, as can be seen in Figure 2. In this study, the amount of lignin added to paint was small and did not influence the drying time.
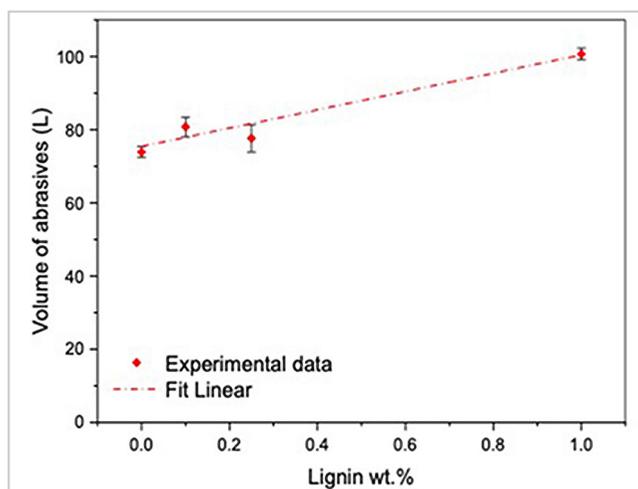

Figure 3 - Variation of the average volume of abrasives (l) in relation to the percentage of added lignin.

Lignin is a rigid, amorphous three-dimensional biopolymer that has relatively numerous hydroxyl functional groups active in hydrogen bonding (Luo et al., 2013). Since the water-emulsified acrylic paint is a polymer with interpenetrating structure, it is inferred that the dispersion of lignin in the acrylic resin forms a complex molecular structure, in which lignin occupies the amorphous phase of the polymer increasing the volume and reinforcing the structure formed in a level molecular. Thus, mixing small amounts of lignin in the paint improved the wear resistance of the resulting product, as can be seen from the increased abrasive volume shown in Figure 3.

In the flexibility test, one of the qualitative requirements of road marking paint, the result obtained was satisfactory. According to Figure 4, there was no cracking or peeling of the paint after folding the plates around the metal cylinder. Lignin contains many benzene rings, methyl groups and a small number of aliphatic groups in the side chain. Such groups present in the lignin structure improve the flexibility of road paint (Yan et al., 2018). However, according to Yan et al. (2018), when the amount of lignin added to the resin is higher than 5.00 wt.%, the amount of benzene rings

and methyl groups increases, which leads to a reduced flexibility. The lignin addition up to 1.00 wt.% in road paint did not affect its flexibility.
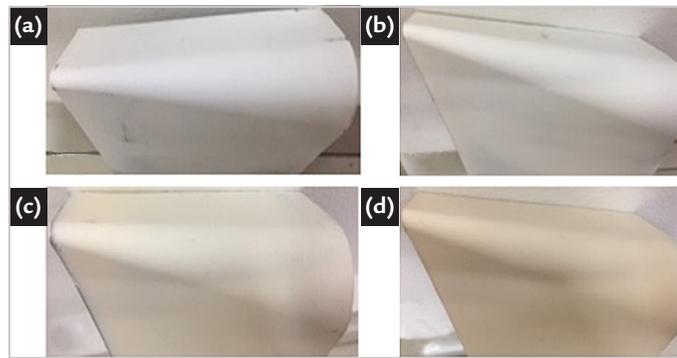

Figure 4 - Road marking paint, after flexibility test, with contents of:
(a) 0 wt.% lignin; (b) 0.10 wt.% lignin; (c) 0.25 wt.% lignin; and (d) 1.0 wt.% lignin

3.2 Accelerated aging resistance test

The oxidative chemical changes in the samples studied are related to the photodegradation and degradation of the paints exposed to the artificial accelerated aging using a Xenon Arc lamp whose spectral range is comparable to the outdoor solar radiation (Bellamy, 1975). Figure 5 and Figure 6 show FTIR spectra of water-based RM paint with lignin addition (0.10, 0.25, and 1.00 wt.%) and without lignin, before and after exposure to the arc xenon lamp radiation.
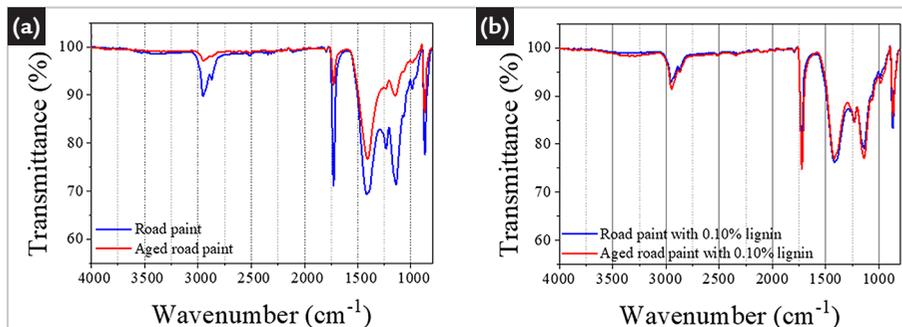

Figure 5 - FTIR spectra of road marking paint and aged road paint containing (a) 0.00 wt.% lignin, (b) 0.10 wt.% lignin.
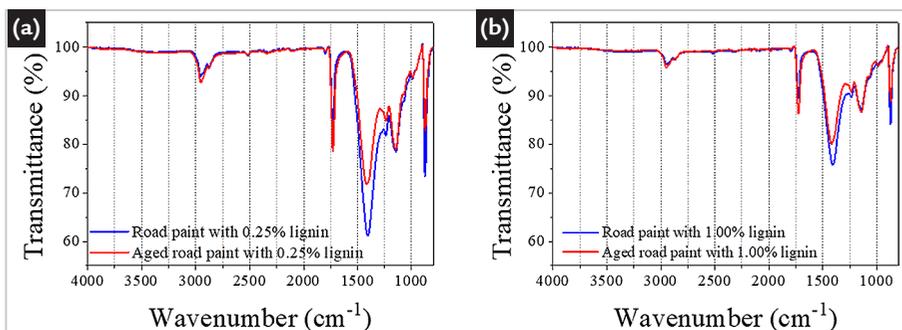

Figure 6 - FTIR spectra of road marking paint and aged road paint containing (a) 0.25 wt.% lignin, and (b) 1.00 wt.% lignin.

The area of each band was determined to provide a semi-quantitative result for degradation analysis. Normalization was done considering the band at 870 cm-1 associated to dolomite as a reference, since this band is not affected by the xenon irradiation. Each area was divided by the area of band ascribed to dolomite. Table 4 shows the ratio of intensity of C-O, C-H and C=O bands ascribed to C-O ($I(C-O/870)$), C-H ($I(CH/870)$) bending and C=O ($I(C=O/870)$).

Table 4 - Ratio of intensity of bands ascribed to
C-O ($I_{(C-O/870)}$), C=O ($I_{(C=O/870)}$), and C-H ($I_{(CH/870)}$) bending before and after the weathering test.

% Lignin	$I_{(C-O/870)}$ BEFORE	$I_{(C-O/870)}$ AFTER	$I_{(C=O/870)}$ BEFORE	$I_{(C=O/870)}$ AFTER	$I_{(C-H/870)}$ BEFORE	$I_{(C-H/870)}$ AFTER
0.00	3.88	2.32	1.53	0.90	1.20	2.41
0.10	3.81	4.50	1.60	2.29	1.18	1.50
0.25	2.77	3.52	0.87	1.67	0.71	1.17
1.00	2.75	3.29	1.00	1.68	0.75	1.07

Melo *et al.* (1999) reported that the main mechanism of photodegradation of acrylic resin is scission of the ester group which causes a decrease in intensity of band at 1027 cm^{-1}. In this study, the intensity of band at 1142 cm^{-1} ascribed to C-O of esters decreased by 40% after aging of the road paint without lignin addition, indicating a scission of the ester group. Throughout the degradation process, the C-O bands of the ester decreased which suggests that reactions on the side chains occurred (Forsthuber and Grüll, 2010). Adding 0.10 wt.%, 0.25 wt.% and 1.00 wt.% of lignin in paint, the intensity of C-O band increased, indicating a beneficial effect of lignin in the photodegradation resistance of paint, since the results suggest that a scission of ester group did not occur.

Anghelone *et al.* (2017) reported that the decreasing of the intensity of carbonyl band is due to the side-chain scission reactions. A decrease of 41% in intensity of the carbonyl band was observed for the RM without lignin addition after the weathering test, indicating that side-chain scission reactions may have occurred. The lignin-modified road marking paint showed an increase in the carbonyl band after weathering aging, indicating the absence of side-chain scissions during aging.

Forsthuber and Grull (2010) reported that the general decrease of the carbonyl band in degradation of acrylics may be due to the abstraction of CO_2. Lignin-modified road marking paint showed an increase in intensity of the band associated to the carbonyl group, indicating the absence of this aging mechanism in RM paint.

Chiantore *et al.* (2000) associated the decrease in intensity of bands of acrylic resin in the region 2800 cm^{-1} to the loss of low molecular weight material generated by photodegradation. Absorptions at 2800 cm^{-1} showed a slight increase after aging for lignin-modified paints (Figure 5 and Figure 6). Only the road marking paint without lignin showed a decrease in intensity of bands at 2800 cm^{-1}, indicating a photodegradation with a loss of low molecular weight material (Fig. 5 and Fig.6).

The variation in the fingerprint region between 1400 and 700 cm^{-1} may be attributed to the loss of low molecular weight material formed during the degradation (Chiantore *et al.*, 2000). The road paint without lignin addition showed a decrease of intensity of bands in the fingerprint region between 1400 cm^{-1} and 700 cm^{-1}, as shown in Figure 5. However, the lignin-modified paint showed a much lower variation of the intensity of the

bands in this region (Figure 5 and Figure 6). The reactions promoted by the high-energy radiation (higher than 290 nm) are homolyzes of all types of chemical bonds, bringing the polymer structure to complete fragmentation (Melo *et al.*, 1999).

The absence of any absorption at 1640 and 909 cm^{-1} in the IR spectra shows no formation of vinyl unsaturation during degradation. A similar result was observed by Chiantore *et al.* (2000) that carried out a systematic investigation on the photooxidative stability under conditions of artificial solar light irradiation of acrylic and methacrylic based polymers.

Considering two important indicators of degradation of the acrylic resin, which are the reduction of the intensity of the band associated with C-O of the ester group, and the decrease of the intensity of band related to the carbonyl group C=O and considering that the intensities of such bands decreased by 40% for unmodified paint while increasing after aging for lignin-modified paint, a gain of about 40% in the service life of the paint can be inferred.

Another important finding of this work was that only the road marking paint without lignin showed a decrease in intensity of bands at 2800 cm^{-1}, indicating a photodegradation with a loss of low molecular weight material.

3.3 Color change

Table 5 shows the color analyzes of the samples with and without the addition of lignin, before (initial value) and after (final value) the aging tests. The following parameters are represented in them: L * (light / dark), a * (green / red), b * (yellow / blue) and ΔE * (color variation). The lignin, when added to the paint,

makes it darker, reddish, and yellow, according to the values of the parameters L *, a * and b * shown in Table 5. The addition of lignin mainly decreased L *, making the white paint yellowish and, as such, not really usable. This is a relevant result that should direct the research to yellow paints in the future.

The general behavior of the paints analyzed with lignin, after artificial accelerated aging, was an increase in L *, corresponding to a lightening of the pigment during aging, and a systematic tendency to decrease the b * and a * parameters. Such lightening and consequent increase in the brightness

Table 5 - CIELAB parameters of lignin-modified road marking paint before and after aging.

	% Lignin	L*	a*	b*	ΔE*
Before		96.07	-0.82	1.44	
After	0.0	93.78	-1.19	6.33	5.41
Δ		-2.29	-0.37	4.89	
Before		91.67	0.28	10.69	
After	0.10	94.20	-1.22	4.87	6.52
Δ		2.53	-1.50	-5.82	
Before		87.82	1.67	13.20	
After	0.25	94.04	-1.35	4.62	11.02
Δ		6.22	-3.02	-8.58	
Before		81.64	2.50	15.07	
After	1.00	93.17	-1.36	5.97	15.19
Δ		11.53	-3.86	-9.10	

of the samples can be attributed to the smoothing of the film surface during exposure to UV radiation. It should be noted that RM paints are designed to furnish a relatively rough surface. The higher the percentage of lignin added to the road marking paint, the greater the color variation observed. Acrylic polymers, due to photodegradation, may have their tonality changed, becoming more yellow. This consequence can be attributed to the formation of conjugated double bond systems (Melo *et al.*, 1999). The addition of lignin in the asphalt demarcation paint delayed the yellowing of the aged samples. As can be seen in Table 5, with the addition of lignin, the samples become bluer (negative Δb), while the paint without lignin becomes yellower after exposure to radiation. The color variation in the additive road marking paint is mainly due to the release of C = O groups due to the photodegradation of lignin (Pandey, 2005). Although the addition of lignin increases the value of b and the yellowing of the paint, after aging, the lignin has a beneficial effect, contributing to the reduction of yellowing. With the addition of 1.00% lignin, Δb is 13.63. However, with the addition of 1.00% lignin, after aging, Δ b = -9.10, while for the road paint without lignin Δ b = + 4.89.

4. Conclusions

The lignin incorporation improved the lifetime and photostability of water-based road marking paint and no significant changes in the physical chemistry, and the flexibility and no-pick-time test were verified.

The addition of 1.00 wt. % of lignin increased the abrasion resistance by 36%.

Several photodegradation parameters indicated a higher photodegradation resistance of lignin-modified road marking paints. Decreasing of 40% and 41% in intensity of the C-O band and the carbonyl band was observed for the road paint without lignin addition after the weathering test, respectively, indicating that the ester group and side-chain scissions may have occurred, while the intensity of C-O and carbonyl bands increased after aging for lignin-modified water-based road marking paints. Only the road marking paint without lignin showed a decrease in intensity of bands at 2800 cm^{-1}, indicating a photodegradation with a loss of low molecular weight material.

According to the Brazilian standard 15405 - Road Horizontal Signage - Paints - Procedures for the execution of the demarcation and evaluation, the average width and thickness of the paint applied to the pavement should be 15000 μm and 400 μm, respectively. Considering the paint used in this study, 22.92 million tons of paint would be required to maintain each horizontal road mark in Brazil. If 1% lignin is added to asphalt demarcation paints, it will be possible to reduce approximately 229.25 thousand tons of waste from the pulp and paper industries.

Although the addition of lignin increases the yellowing of the paint, making it unfeasible to add it on white RM paint, the lignin has a beneficial effect after aging, contributing to the reduction of yellowing.

This research consisted of a preliminary study of the effect of adding lignin on the photodegradation resistance of the paint. The project must contemplate in subsequent: glass bead adhesion, the possibility of obtaining adequate retro-reflectivity, the in-can stability, the modification of the paint balance by post-addition of lignin, and the study of various types of paint.

References

ANGHELONE, M.; JEMBRIH-SIMBÜRGER, D.; PINTUS, V.; SCHREINER, M. Photostability and influence of phthalocyanine pigments on the photodegradation of acrylic paints under accelerated solar radiation. *Polymer Degradation and Stability*, v. 146, p. 13-23, 2017.

ARO, T.; FATEHI, P. Production and application of lignosulfonates and sulfonated lignin. *ChemSusChem*, v. 10, p. 1861-1877, 2017.

BAJWA, D. S.; POURHASHEM, G.; ULLAH, A. H.; BAJWA, S. G. A concise review of current lignin production, applications, products and their environmental impact. *Industrial Crops and Products*, v. 139, n. 111526, 2019.

BALASUNDRAM, N.; SUNDRAM, K.; SAMMAN, S. Phenolic compounds in plants and agri-industrial by--products: antioxidant activity, occurrence, and potential uses. *Food Chemistry*, v. 99, p. 191-203, 2006.

BATISTA, K. B.; PADILHA, R.; CASTRO, T.; SILVA, C.; ARAÚJO, M. F. A.; LEITE, L. M. F.; PASA, V. D.; LINS, V. F. C. High-temperature, low-temperature and weathering aging performance of lignin modified asphalt binders. *Industrial Crops and Products*, v. 111, p. 107-116, 2018.

BELLAMY, L. *The infrared spectra of complex molecules*. London: Chapman and Hall, 1975.

BREWER, M. Natural antioxidants: sources, compounds, mechanisms of action, and potential applications. *Comprehensive Reviews in Food Science and Food Safety*, v. 10, p. 221-247, 2011.

BURGHARDT, T. E.; PASHKEVICH, A. Emissions of volatile organic compounds from road marking paints. *Atmosphere Environment*, v. 193, p. 153-157, 2018.

CHEN, Z.; WAN, C. Biological valorization strategies for converting lignin into fuels and chemicals. *Renewable & Sustainable Energy Reviews*, v. 73, p. 610-621, 2017.

CHIANTORE, O.; TROSSARELLI, L.; LAZZARI, M. Photooxidative degradation of acrylic and methacrylic polymers. *Polymer*, v. 41, p. 1657, 2000.

CONFEDERAÇÃO NACIONAL DO TRANSPORTE. *Anuário CNT do transporte*: estatísticas consolidadas. [*S. l.*]: CNT, 2019. Available at: https://anuariodotransporte.cnt.org.br/2019/. Accessed: 30 June 2020.

CRUZ, M.; KLEIN, A.; STEINER, V. Sustainability assessment of road marking systems. *Transportation Research Procedia*, v. 14, p. 869-875, 2016.

FATEMI, S.; VARKANI, M. K.; RANJBAR, Z.; BASTANI, S. Optimization of the water-based road-marking paint by experimental design, mixture method. *Progress in Organic Coatings*, v. 55 p. 337-344, 2006.

FORSTHUBER, B.; GRÜLL, G. The effects of HALS in the prevention of photo-degradation of acrylic clear topcoats and wooden surfaces. *Polymer Degradation and Stability*, v. 95, p. 746-755, 2010.

HADIZADEH, E.; PAZOKIFARD, S.; MIRABEDINI, S. M.; ASHRAFIAN, H. Optimizing practical properties of MMA-based cold plastic road marking paints using mixture experimental design. *Progress in Organic Coatings*, v. 147, n. 105784, 2020.

LUO, X.; MOHANTY, A.; MISRA, M. Lignin as a reactive reinforcing filler for water-blown rigid biofoam composites from soy oil-based polyurethane. *Industrial Crops and Products*, v. 47, p. 13-19, 2013.

MELO, M.; BRACCI, S.; CAMAITI, M.; CHIANTORE, O.; PIACENTI, F. Photodegradation of acrylic resins used in the conservation of stone. *Polymer Degradation and Stability*, v. 66, p. 23-30, 1999.

MIRABEDINI, S. M.; ZAREANSHAHRAKI, F.; MANNARI, V. Enhancing thermoplastic road-marking paints performance using sustainable rosin ester. *Progress in Organic Coatings*, v.139, n.105454, 2020.

NANCE, J.; SPARKS, T. D. From streetlights to phosphors: A review on the visibility of roadway markings. *Progress in Organic Coating*, v. 148, n. 105749, 2020.

PANDEY, K. K. Study of the effect of photo-irradiation on the surface chemistry of wood. *Polymer Degradation and Stability*, v. 90, p. 9-20, 2005.

PASHKEVICH, A.; BARTUSIAK, J.; ŻAKOWSKA, L.; BURGHARDT, T. E. Durable waterborne horizontal road markings for improvement of air quality. *Transportation Research Procedia*, v. 45, p. 530-538, 2020.

PINTUS, V.; WEI, S.; SCHREINER, M. UV ageing studies: evaluation of lightfastness declarations of commercial acrylic paints. *Analytical and Bioanalytical Chemistry*, v. 402, p. 1567-1584, 2012.

YAN, R.; YANG, D.; ZHANG, N.; ZHAO, Q.; LIU, B.; XIANG, W.; SUN, Z.; XU, R.; ZHANG, M.; HU, W. Performance of UV curable lignin based epoxy acrylate coatings. *Progress in Organic Coatings*, v. 116, p. 83-89, 2018.