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ORIGINAL PAPER

Contribution to the Study of Fungal Attack on Some Plasticized Vinyl Formulations

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Abstract The objective of this study was to develop new vinyl flooring formulations with increased resistance to fungi and microorganisms attack, by using plasticizers having a chemical composition different from that of common di-ethylhexyl phthalate (DOP). It is suspected that during the vinyl flooring life service, the attack of fungi and microorganisms leads to the degradation of DOP and the release of some volatile organic compounds (VOC). For this reason the new materials were formulated with plasticizers having chemical composition different of that of DOP i.e.: diethyleneglycol dibenzoate (2–45), tricresyl phosphate (Lindol) and phenol alkylsulphonic ester (Mesamoll). For the same reason in the new flooring formulations the vinyl polymer, vinyl chloride-vinyl acetate copolymer (VC-VAc), was partially replaced with lignin (L) a natural polymer and major component of wood and vascular plants. Besides its other functions in wood, L imparts resistance to the most microorganisms attack. An organosolv lignin Alcell lignin (AL) was utilized as partial replacement of VC-VAc copolymer.

The influence of the new plasticizers, as well as the influence of the partial replacement of VC-VAc copolymer with L on the resistance of the new formulations to fungal attack was evaluated following a standard procedure given in ASTM G 21–2002 ''Determining Resistance of Synthetic Polymeric Materials to Fungi''. The evaluation has been undertaken for controls (formulated without AL) and blends (formulated with 20 parts AL) specimens. Test specimens were inoculated with a mixture of five fungi. Following 28 days of incubation at 28°C and 95% relative humidity, the specimens were examined visual and under the microscope and rated for fungal growth. Weight loss, changes in mechanical properties and changes in glass transition temperature due to the effect of biodeterioration were also determined.

Although each plasticizer has a specific resistance to hydrolysis due to differences among ester groups, the visible effects of fungal attack, in formulations without AL, is similar for all plasticized controls, with the exception of formulations incorporating diethyleneglycol dibenzoate (2–45) in which a higher degree of biodegradation was always present. Based on the weight loss of specimens formulated without AL, their resistance to fungal attack can be rated as follows: $\text{Lindol} > \text{Mesamoll} \geq \text{DOP} > 2-45$. The same rating is applicable for blend specimens. The results have demonstrated that each particular AL-plasticizer-additives formulation has its specific mechanism of biodegradation.

Keywords Fungal resistance · Plasticized VC-VAc copolymer · Plasticized VC-VAc copolymer-lignin blends · Vinyl flooring biodegradation

Introduction

Resilient flooring obtained from plasticized poly (vinyl chloride) (PVC) or vinyl chloride (VC) with vinyl acetate

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(VAc) copolymer is characterized by high impact resistance, stiffness and toughness even at a filler loading in the range of 200 parts per hundred parts resin (phr).

General purpose plasticizers such as diisoheptyl phthalate (DIHP), di-ethylhexyl phthalate (DOP), and diisononyl phthalate (DINP) are currently used at 50–100% of the plasticizers system in formulations for vinyl tiles [1].

Plasticized VC homopolymer and VC copolymers, especially with VAc have been used for more than 40 years without a single known environmental effect of plasticizers degradation. These additives have been traditionally considered to be inert and non-volatile. However, among the major thermoplastic materials, plasticized PVC is the most susceptible to microbiological attack particularly due to the presence of plasticizers. The most significant degradative organisms are fungi of many different types. Fungi have been shown to produce enzymes capable of totally or partially breaking the ester linkages present in most of plasticizers into more volatile components. These components are subsequently released into the enclosed building environment and may thus subject its' occupants to long-term exposure of low levels of volatile organic compounds (VOC) [2].

Webb et al. showed that plasticization with DOP and dioctyl adipate (DOA) increases adhesion of deteriogenic fungus *Aureobasidium pullulans* to plasticized PVC and stimulates its biodegradation. This fungus is omnipresent within the environment and is known to colonize many habitats [3].

Gumargalieva et al. [4] showed that the loss of a dialkyl phthalate (not specified) plasticizer for PVC under the influence of surface biodegradation by the microscopic fungus *Aspergillus niger* is much faster than the loss without fungal overgrowth. In the absence of fungus, the loss rate is limited by the volatility of the plasticizer, whereas in the presence of fungus, it is limited by the diffusion of the plasticizer. Therefore, the fungus acts like a leaching solvent, presumably because it effectively removes the plasticizer from the surface of the material by biodegradation.

The relative susceptibility of esters to microbial attack is influenced, in the same manner as their relative susceptibility to hydrolysis, by steric factors that, dictate the strength of the ester groups. Fungi have been shown to produce esterases, the enzymes capable of breaking the ester linkages. The fragment molecules so produced can then be metabolized by fungi. The plasticizer biodegradation is especially prevalent in humid environments. Staining, commonly pink color is a result of bacterial activity. The familiar odor of mildew growth may also occur, as well as plasticizer decomposition products [5].

Concerns over VOC emissions of plasticized PVC, point to the need for research of more sustainable alternatives to PVC based building materials. In this respect new flooring formulations incorporating other plasticizers that have chemical compositions different from that of the commonly used dialkyl phthalates were investigated in our laboratory. In addition, for the proposed new flooring material formulations, the vinyl copolymer was partially replaced with lignin (L), a natural occurring polymer, and one of the major components of wood. Lignin imparts rigidity to wood cells, creating a composite material that is resistant to external forces and to most microorganisms attack [6]. White rot fungi are the only microorganisms that degrade L to any substantial degree [7]. They belong to the group of three fungi, which decay wood, and in contrast to other two (soft-rot and brown-rot fungi), they are capable of degrading not only cellulose and hemicelluloses but L also.

L molecules are composed of phenyl propane units interconnected by about ten different linkages in a complex matrix. This matrix consists of a variety of functional groups, including hydroxyl, methoxy, and carbonyl units, which impart polarity to the L macromolecules [7].

Because of the complex structure of native L, and its abundance, interest in the development of L blends containing synthetic polymers was been almost continuous in the past 20 years, but in most of the cases, the resulting materials were brittle and weak, with poorly defined thermal transitions.

Recently published data show that generally the mechanical properties of L-synthetic polymer blends are strongly influenced by the degree of association of the L components [8]. Indeed, although the molecular weight of L ranges from 1000 to 12,000 its glass transition temperature (T_g) is between 100 and 180°C, which is high compared with the T_g's of most synthetic materials. According to Yoshida et al. [9], the high T_g values of L are due, in large part, to the degree of association by hydrogen bonding caused by the presence of phenolic hydroxyl groups in the main chains.

Studies done in our laboratory [10] have demonstrated that it is possible to reduce the T_g of L and, consequently, the degree of association between the individual molecular components through the use of specific plasticizers. These studies had indicated that the compatibility and efficiency of a plasticizer toward L is strongly influenced by its solubility parameter. This one is generally a useful guide to predicting compatibility. Frequently, a polymer will be compatible with a plasticizer when the two have solubility parameters that do not differ by more than $\pm 1.5\ (\mathrm{cal/cm^3})^{1/2}$ [11]. As the solubility parameter of L is $\cong 10\ (\mathrm{cal/cm^3})^{1/2}$ [12], plasticizers with a high solubility parameter were selected for the present study. Others criteria in selecting the plasticizers for the study was their compatibility with the vinyl copolymer and a chemical composition that render the ester group more stable to hydrolysis than in alkyl phthalates.

These plasticizers were: diethyleneglycol dibenzoate (2–45), tricresyl phosphate (Lindol) and phenol alkylsulphonic ester (Mesamoll).

The present work was undertaken with an organosolv L, Alcell (AL). It is obtained through a new delignification process, and it is in a less unaltered form than the lignins obtained by sulphate or sulphite process.

All the studied plasticizers are compatible with VC-VAc copolymer. Lindol, as a triaryl phosphate is known for its good microbial resistance [13]. Our studies indicated that it is an efficient plasticizer for AL [10]. The phenyl sulphonate ester group from Mesamoll has a low susceptibility to hydrolysis and, consequently, good microbial resistance [5]. Although it has a high solubility parameter its compatibility with AL is rather poor [10]. Due to the bulky structure of 2–45, the carbonyl groups of this plasticizer are not readily accessible to H^+ or OH^- (acidic or basic hydrolysis) and it was expected that its fungal attack will be very slow. In addition this compound is a very good plasticizer for AL [10].

In this paper an analysis of several plasticized vinyl copolymer-AL blends used as matrices for a high level of calcium carbonate filler in a vinyl tile composite is done. The study focuses on the influence of different plasticizers (having chemical compositions that differed from that of the more commonly used dialkyl phthalates), as well as the influence of partial replacement of the vinyl copolymer with AL, on the stability of the formulations to fungal attack. Although DOP is not compatible with AL [10], controls and blends formulated with this plasticizer have been prepared for comparison because it is the plasticizer of choice in vinyl tile formulations [5].

Experimental

Procedures

The basic component for the formulations was a copolymer VC-VAc with 9.7 wt% VAc that is mostly used in vinyl flooring formulations. The blends incorporated AL. Controls with 100 parts VC-VAc and blends containing 80 parts VC-VAc and 20 parts AL were formulated with 35 phr plasticizer, 200 phr calcium carbonate filler, 3 phr dibutyltin dilaurate heat stabilizer and 1.5 phr calcium stearate lubricant. The following plasticizers were utilized: DOP, tricresyl phosphate (Lindol), phenol alkyl sulphonic ester (Mesamoll) and diethyleneglycol dibenzoate (2–45). The characteristics and the manufacturers of all the above-mentioned materials have previously been published [10]. The controls and blends formulations were obtained by melt mixing and compression molding following a previously described procedure [14]. It consists in melt mixing of each dry blend formulation for eight minutes at 141°C and a rotor speed of 65 rpm, in a Haake Rhemix 600 equipped with roller blades. Thereafter the material was ground and subsequently sheets of 1.5 mm thickness were molded by compression at 153°C and 4.37 MPa in a Carver Pres. The molded sheets were cooled in the mold at room temperature at a cooling rate of 10°C/min.

Two sheets of 7 × 13 × 0.15 cm were prepared for each formulation and tested for resistance to fungal attack following a standard procedure given in ASTM G 21–2002 (''Determining Resistance of Synthetic Polymeric Materials to Fungi''). This test employs a mixed fungal spore suspension containing the following fungi: *Aspergillus niger* (ATCC #9642), *Penicillium pinophilum* (ATCC #11797), *Chaetomium globosum* (ATCC #6205), *Gliocladium virens* (ATCC# 9645) and *Aureobasidium pullulans* (ATCC #15233). A sterile sheet from each formulation was placed on a mineral salts agar medium and inoculated with a suspension containing a mixture of the five fungi spores. This represents the inoculated specimen (IS). After 28 days of incubation at 28°C and 95% relative humidity (RH) the specimens were examined and rated for fungal growth. Another sterile sheet from each formulation was incubated in similar conditions but without fungal inoculation. This represents the sterile specimen (SS). The results of these preliminary tests indicated that the fungal growth was similar on all the surfaces of control specimens (less than 10%), except those formulated with 2–45 plasticizer, where the fungal growth was of about 20%. These results were quite surprising because, as it was discussed in the Introduction, alkyl sulphonic phenyl ester group present in Mesamoll should have a higher resistance to hydrolysis and consequently to fungal attack as compared to aryl phosphate ester present in Lindol and much higher than alkyl carbonyl ester present in DOP. Also, as it was pointed above, the chemical composition of 2–45 should render it more resistant to hydrolysis—and fungal attack—than DOP. The results suggested that other additives present in these formulations could be targets for fungal attack. The heat stabilizer, dibutyltin dilaurate, and the calcium stearate lubricant, both derivatives of fatty acids, were suspected to enhance the adhesion of fungi to exposed surfaces due to the fungi's affinity for fatty acids derivatives [15, 16].

Consequently new formulations were prepared in the same conditions and proportions as described above, the only difference consisting in the chemical nature of the heat stabilizer and lubricant. As a substitute for dibutyltin dilaurate a butyltin mercaptide/carboxylate (Mark TK 262 GV, obtained from Crampton Vinyl Additives GmbH, Germany) was used with a paraffin wax (Marklube 367-same company as heat stabilizer) as external lubricant. Controls and blends were formulated with the previous heat stabilizer and lubricant (Formulation I) as well as with

Table 1 Composition (in phr) and designation of tested formulations

	Controls				Blends			
Formulation components/designation	I	IA	II	IIA	I	IA	II	IIA
VC-VAc resin	100	100	100	100	80	80	80	80
Alcell lignin	0	0	0	0	20	20	20	20
Plasticizer DOP or Mesamoll or Lindol or 2–45	35	35	35	35	35	35	35	35
Ca Carbonate filler	200	200	200	200	200	200	200	200
DBTDL* heat stabilizer	3	3	0	0	3	3	0	0
Ca Stearate lubricant	1.5	1.5	0	0	1.5	1.5	0	0
Mark TK 262 heat stabilizer**	0	0	3	3	0	0	3	3
Marklube 367 lubricant***	0	0	1.5	1.5	0	0	1.5	1.5
Sanitzed PL-21–60 biocide****	0	2	0	2	0	2	0	2

*Dibutyltin dilaurate

**Butyltin mercaptide/carboxylate

***Paraffin wax

****Phyrithion compound

the new ones (Formulation II). In addition, other compositions were formulated on the basis of the old and new set of heat stabilizer and lubricant with a biocide in proportion of 0.6% calculated on the weight of final product (Formulations IA and IIA). The biocide was Sanitized PL-21–60 (produced by Clariant Huningue S.A., Switzerland). It is a plastisol containing a pyrithyon compound. The components of each formulation as well as the designation of each formulation are presented in Table 1. A total of 16 formulations representing control specimens and 16 formulations representing blends specimens were prepared and the working procedures were similar as in the preliminary tests mentioned above.

Three sheets (7 × 13 × 0.15 cm) were pressed for each formulation. Two out of three sheets were inoculated with the fungal suspension (inoculated specimens IS) and incubated for 28 days at 28°C and 95% RH. After the incubation period, each sheet was examined for fungal growth then disinfected with a solution of mercuric chloride, washed and dried at room temperature for 24 h. One of each sheet was dried for another 6 days and thereafter five dumbbell shaped specimens were cut and tested for tensile properties. The remaining sheet was used for determining the weight loss. The non-inoculated sheets (sterile specimens, SS) were incubated at similar conditions. After the incubation period, the sheets were examined for fungal growth and after 6 days drying, five dumbbell shaped specimens were cut and tested for tensile properties.

The susceptibility of control and blend specimens of all the formulations to fungi attack has been evaluated by the determination of:

- intensity of fungal growth;
- loss in weight;
- changes in mechanical properties (elastic modulus, tensile strength at yield and break, elongation at break);
- glass transition temperature (T_g).

Testing

The intensity of fungal growth was determined by visual examination of specimens following 28 days incubation, and confirmed under the microscope examination at 50× magnification (Wild M5A Microscope) in accordance with ASTM G21–2002.

The fungi rating according to this ASTM is presented in Table 2.

For determining the loss in weight, prior to inoculation, all specimens (whose weight was of about 25 g), were weighted to the nearest 1 mg. After the incubation period and rating for the degree of fungal growth, the specimens were washed with a solution of mercuric chloride and rinsed with water. The surface water was removed with adsorbent paper. The samples were dried at room temperature until constant weight was achieved.

The percentage of loss in weight after the incubation period was calculated as follow:

$$\%\ \text{Loss in weight} = [(W - W_1)/W] \times 100$$

Table 2 Fungi rating according to ASTM G21–2002

Observed growth on specimens (sporulating or non-sporulating or both)	Rating
None	0
Traces of growth (less than 10%)	1
Light growth (10–30%)	2
Medium growth (30–60%)	3
Heavy growth (60% to complete coverage)	4

where W = weight of the test specimen before inoculation, W_1 = weight of the specimen after incubation period and subsequent drying to constant weight.

After drying, from each inoculated and sterile sheet, five dumbbell shaped specimens were cut and used for tensile testing and the indicated values of tensile tests are representative of an average derived from five specimens. The tensile tests were completed according to ASTM D 638M-2003 ''Standard Test Method for Tensile Properties of Plastics (Metric)'' using an Instron Universal Testing Machine at a cross speed of 15 mm/min. The elastic modulus was determined at 2% elongation.

From the same sheets samples of about 20 mg were punched and tested for determination of T_g. This was done on a Differential Scanning Calorimeter (TA Instrument) at a heating rate of 20°C/min under nitrogen atmosphere between −50 and 160°C. The reported values of T_g were estimated from the second calorimetric run. At least two specimens were run from each sheet.

Results and Discussion

Fungal growth rating

The fungal growth rating of all the inoculated specimens is presented in Table 3. As was expected, and observed in the preliminary tests, the fungal growth in Formulation I covered less than 10% of the surfaces of all control specimens with the exception of the control specimens plasticized with 2–45. The fungal growth was more visible on the surfaces of specimens derived from blends formulations. The presence of the biocide (Formulation IA) seems to prevent fungal growth on all surfaces of control specimens. However, traces of fungal growth were observed on the surfaces of specimens from blended formulations plasticized with DOP and Mesamoll. All the control specimens obtained with Formulation II (except those plasticized with 2–45) did not show traces of fungal growth. This observation could confirm the fact that the heat stabilizer and/or the lubricant, both derivatives of fatty acids, are the principal target of fungal attack in Formulation I. Nevertheless, the new additives do not seem to be effective for blends obtained with Formulation II; in this case the fungal growth rating is similar to that observed in Formulation I. Therefore, one may presume that in all the blends the lignin is the favored fungal carbon source. The biocide added in Formulation II, (i.e. Formulation IIA), appears to be more efficient than in Formulation I. From the entire set of specimens examined (Table 3) and derived from blended formulations, only those plasticized with 2–45 presented a light fungal growth.

Table 3 Specimen surface fungal growth rating after an incubation period of 28 days

Sample identification	Formulation			
	I	IA	II	IIA
DOP control	1	0	0	0
DOP blend	3	1	3	0
Mesamoll control	1	0	0	0
Mesamoll blend	3	1	3	0
Lindol control	1	0	0	0
Lindol blend	1	0	2	0
2–45 control	2	0	1	0
2–45 blend	4	0	4	2

Loss in weight

The weight loss data after a 28-day incubation and subsequent drying periods are shown in Table 4. The same table also shows the percentages of weight increase after the 28-days incubation period, that, in effect, represent the percentages of water absorption over this period as a consequence of the high humidity level (95% RH) specified in ASTM.

As can be seen from this table, the weight loss values for all the control specimens following the drying period are very small, close to 0.1–0.2%, except the controls formulated with 2–45 plasticizer. As compared to the control specimens, the weight loss for all the blend specimens is slightly higher, as it was higher too the intensity of fungal growth on theirs surfaces. In general, but with some exceptions, there is a slight decrease of the weight loss for all the specimens formulated with the biocide. This observation indicates that it is able to provide an enhanced resistance to biodegradation.

The drying time was quite long, ranged between 5 and 15 days, depending on the type of formulation; as a general trend it was higher for specimens formulated with the biocide, and higher for blends as compared to control specimens. The presence of high amounts of calcium carbonate filler could be responsible for the different times of drying, due to different water absorption and desorption levels within the filler, as result of its dissimilar degrees of dispersion in each formulation. It is likely as well that the polymer matrix becomes more compact over the incubation period as a result of the ASTM specified incubation temperature (28°C) over the 28-day period; this temperature was in most of the cases higher than the T_g of polymer matrix as can be seen from Table 10. This more compact structure would likely cause a reduction of the rate of water desorption from the material. The changes that occur in the material structure due to the effects of temperature and time will be discussed later. All the tested specimens contain 58.9% mineral filler and 29.5% vinyl polymer, both components being resistant to biodeterioration. A rough estimate of the loss in weight of plasticizer and additives

Table 4 Increase and loss in weight after 28-day incubation period and subsequent drying of control and blend specimens expressed as percentages of initial weight

Sample identification	Formulation I Weight incr. %	I Weight loss %	IA Weight incr. %	IA Weight loss %	II Weight incr. %	II Weight loss %	IIA Weight incr. %	IIA Weight loss %
DOP control	0.503	0.119	0.488	0.103	1.637	0.093	1.324	0.093
DOP blend	0.863	0.197	1.076	0.186	0.859	0.197	0.894	0.155
Mesamoll control	0.518	0.128	0.479	0.094	1.358	0.096	1.667	0.085
Mesamoll blend	0.914	0.204	1.119	0.211	0.868	0.170	0.945	0.168
Lindol control	0.245	0.075	0.233	0.035	1.145	0.130	1.487	0.128
Lindol blend	0.423	0.200	0.450	0.163	1.652	0.198	0.914	0.148
2–45 control	0.115	0.298	0.169	0.208	2.099	0.302	2.719	0.286
2–45 blend	1.105	0.584	1.336	0.440	1.142	0.790	1.509	0.609

was obtained by reporting the values of loss in weight for all the control specimens of Formulation I and IA to the content of plasticizer and additives in the respective formulations. A similar estimation was made for the control specimens obtained with the Formulation II and IIA, but in this case the total weight loss was reported to the plasticizer content only, presuming that the other additives were not affected by the fungi mixture as was described above. Given that AL is likely deteriorated by fungi, an estimate of the AL deterioration was calculated by reporting the difference loss in weight between blend and respective control. All these estimates are presented in Table 5.

Mechanical properties

The mechanical properties and the % changes of these properties as a consequence of the biodegradation process of inoculated and sterile control specimens, after a 28-days incubation period, are presented in Tables 6–9. The following data are presented: modulus at 2% elongation, tensile strength at yield and break and % elongation at break.

The % changes for each property was calculated according to the formula:

$$\% \text{ Change} = [(\text{IS Data} - \text{SS Data})/\text{SS Data}] \times 100$$

where IS Data represents the tensile test value of the inoculated specimen, SS Data represents the tensile test value of the sterile specimen.

The effect of fungal attack on the mechanical properties of the IS will be discussed later.

The values of T_g for the IS and SS are given in Table 10. Results derived from different test methods including, fungal growth rating, changes in mechanical properties of IS versus SS and differences in the values of T_g of IS and SS (ΔT_g) are presented in Table 11. A discussion concerning these results for each particular plasticized formulation follows:

Effect of plasticizers

DOP in controls

Formulation I: a fungal growth rating of less than 10%, some weight loss, increases in modulus as well as yield and break strength indicate that as the effect of fungal attack this material was degraded to a certain degree. Surprisingly, the ΔT_g is negative. A decrease of the T_g of IS is an

Table 5 Estimated loss in weight percentages of plasticizers and additives for controls in Formulations I and IA, of plasticizers for controls in Formulation II and IIA and of AL for blends in all Formulations

Sample identification	Formulation I Plasticizer and additives loss (%)	IA Plasticizer and additives loss (%)	II Plasticizer loss (%)	IIA Plasticizer loss (%)
Controls				
DOP	1.02	0.89	0.90	0.91
Mesamoll	1.10	0.81	0.93	0.83
Lindol	0.30	0.65	1.26	1.25
2–45	2.56	1.80	2.93	2.79
AL loss, blends (%)				
DOP	1.32	1.42	1.77	1.06
Mesamoll	1.29	2.00	1.26	1.42
Lindol	2.17	2.13	1.15	0.34
2–45	4.86	3.97	8.29	5.52

Estimated % weight loss of plasticizer and additives = [(% total weight loss of the specimen)/(% plasticizer and additives)] × 100; % plasticizer and additives are: 11.63 in Formulation I and 11.56 in Formulation IA

Estimated % weight loss of plasticizer = [(% total weight loss of the specimen)/(% plasticizer)] × 100; % plasticizer are: 10.31 in Formulation II and 10.25 in Formulation IIA

Estimated % weight loss of AL = [(% total weight loss of the blend)–(% total loss weight of the control)]/[(% AL)] × 100; % AL are: 5.89 in Formulations I and II and 5.85 in Formulations IA and IIA

Table 6 Elastic modulus at 2% elongation (in MPa) of control and blend specimens after 28-day incubation period

	Controls			Blends		
Sample ID	SS	IS	% Change	SS	IS	% Change
DOP						
Formulation I	80.7	87.5	8.4	83.8	74.6	−11.0
Formulation IA	96.7	103.7	7.2	93	88.5	−4.8
Formulation II	91.6	110.2	20.3	109.5	111.7	2.0
Formulation IIA	76.6	81.6	6.5	98.4	87.5	−11.1
2–45						
Formulation I	92.8	97.2	−4.5	157.3	178	13.2
Formulation IA	116.9	120	2.7	155.3	159.8	2.9
Formulation II	100.5	130.6	30.0	237.6	272.9	14.9
Formulation IIA	71.8	82.1	14.3	224.1	193.3	−13.7
Lindol						
Formulation I	287.2	304.5	6.0	309.8	327.7	5.8
Formulation IA	258.6	279.3	8.0	303	313.3	3.4
Formulation II	279.2	310.7	11.3	318.6	337.7	6.0
Formulation IIA	236.3	257.7	9.1	281.4	261.9	−6.9
Mesamoll						
Formulation I	–	–	–	–	–	–
Formulation IA	106.8	109.8	2.8	122.3	127.8	4.5
Formulation II	109.6	129.1	17.8	135.4	129.2	−4.6
Formulation IIA	106.4	102.1	−4.0	114.1	109.4	−4.1

indication that the heat stabilizer and lubricant, both fatty acids derivatives, were the fungal nutrients rather than the DOP plasticizer. As can be seen from Table 10, in absence of these additives, respectively in Formulation II, the value of the T_g is sensible lower for control specimen plasticized with DOP. An unexpected slight increase of the elongation at break was observed.

Formulation IA: a fungal growth rating of 0, slightly lower weight loss, lower increases of modulus, strength at yield and break, as compared to Formulation I, accompanied by a slight increase in the T_g and decrease of elongation combine to suggest that the biocide had provided a certain protection without completely preventing biodegradation. However, the slight increase of the T_g would indicate that in this instance the plasticizer rather than the additives is deteriorated, because the values of T_g always correlate with plasticizer levels.

Data taken from the literature [17–20] attest the fact that a visual assessment of fungal growth on a surface is not always in agreement with other methods of evaluating

Table 7 Tensile strength at yield (in MPa) of control and blend specimens after 28-day incubation period

	Controls			Blends		
Sample ID	SS	IS	% Change	SS	IC	% Change
DOP						
Formulation I	4.42	4.59	3.8	3.48	3.13	−10.1
Formulation IA	4.72	4.77	1.1	3.85	3.82	−0.8
Formulation II	5.57	5.97	7.2	–	–	–
Formulation IIA	5.57	5.84	4.8	–	–	–
2–45						
Formulation I	3.84	4.09	6.5	3.99	4.58	14.8
Formulation IA	4.31	4.43	2.8	3.79	4.05	6.9
Formulation II	5.95	6.26	5.2	6.35	6.74	6.1
Formulation IIA	5.47	5.52	0.9	5.91	5.43	−8.1
Lindol						
Formulation I	7.39	7.45	0.8	7.32	7.38	0.8
Formulation IA	6.89	7.15	3.8	7.34	7.06	−3.8
Formulation II	9.11	10.17	11.6	–	–	–
Formulation IIA	8.4	6.38	−24.0	–	–	–
Mesamoll						
Formulation I	–	–	–	–	–	–
Formulation IA	5.25	5.26	0.2	4.48	4.58	2.2
Formulation II	6.3	6.47	2.7	–	–	–
Formulation IIA	6.55	6.38	−2.6	–	–	–

Table 8 Tensile strength at break (in MPa) of control and blend specimens after 28-day incubation period

	Controls			Blends		
Sample ID	SS	IS	% Change	SS	IS	% Change
DOP						
Formulation I	6.1	6.32	3.6	4.17	4.1	−1.7
Formulation IA	6.05	6.42	6.1	4.36	4.44	1.8
Formulation II	5.67	5.81	2.5	8.79	9.24	5.1
Formulation IIA	5.44	5.59	2.8	9.2	8.96	−2.6
2–45						
Formulation I	6.35	6.36	0.2	4.21	4.5	6.9
Formulation IA	6.31	6.69	6.0	4.51	4.51	0.0
Formulation II	6.03	6.04	0.2	4.33	4.06	−6.2
Formulation IIA	5.51	5.51	0.0	3.89	3.98	2.3
Lindol						
Formulation I	7.65	8.09	5.8	5.67	5.72	0.9
Formulation IA	7.78	8.15	4.8	5.6	5.48	−2.1
Formulation II	6.95	9.09	30.8	10	10.13	1.3
Formulation IIA	6.92	8.1	17.1	9.41	9.06	−3.7
Mesamoll						
Formulation I	–	–	–	–	–	–
Formulation IA	6.83	6.87	0.6	4.68	4.69	0.2
Formulation II	6.3	6.31	0.2	8.67	8.85	2.1
Formulation IIA	5.9	5.83	−1.2	9	8.83	−1.9

biodeterioration. Indeed, the fungal growth on a surface of a plastic material can be invisible or uneven. Furthermore, the extent of fungal growth is not always necessarily related to the degree of biodeterioration. On the other hand, the slight deterioration of the material, even in the presence of the biocide, may result from its insufficient inhibitory concentration and on its ability to migrate from the material to the surface. The ability of the biocide to migrate from of the material to the surface will be discussed later.

Formulation II: the fungal growth rating is 0, and in comparison to Formulation I, the weight loss is slightly lower, the T_g increases being indicative of a material having a higher degree of embrittlement; this is clearly evidences of a loss of plasticizer and can be ascribed to physical heterogeneity of the material. In contrast to Formulation I, the level of water absorption was evidently higher. Information obtained from the literature show that, in general, a polymers' resistance to biodegradation, and in particularly that of plasticized PVC, is reduced in

Table 9 Elongation at break (in %) of control and blend specimens after 28-day incubation period

	Controls			Blends		
Sample ID	SS	IS	% Change	SS	IS	% Change
DOP						
Formulation I	273	285	4.4	212	209	−1.4
Formulation IA	264	252	−4.5	216.1	204	−5.6
Formulation II	231	212	−8.2	35	38	8.6
Formulation IIA	247	329	33.2	40	42	5.0
2–45						
Formulation I	287	283	−1.5	214	207	−3.3
Formulation IA	284	278	−2.1	269	258	−4.1
Formulation II	239	194	−18.8	209	158	−24.4
Formulation IIA	272	252	−7.4	216	245	13.4
Lindol						
Formulation I	132	171	29.5	121	104.7	−13.5
Formulation IA	182	176	−3.3	128	148	15.6
Formulation II	87	95	9.2	6	6	0.0
Formulation IIA	114	93	−18.4	10	10	0.0
Mesamoll						
Formulation I	–	–	–	–	–	–
Formulation IA	276	264	−4.3	187	171	−8.6
Formulation II	231	200	−13.4	29	30	3.4
Formulation IIA	180	202	12.2	34.8	35.5	2.0

Table 10 T_g (in °C) of control and blend specimens after 28-day incubation period

	Formulation							
	I		IA		II		IIA	
Sample identification	SS	IS	SS	IS	SS	IS	SS	IS
DOP control	22.5	21.3	21.0	21.9	16.9	19.1	14.4	–
DOP blend	12.4	14.5	11.8	12.1	12.6	12.8	10.4	–
Mesamoll control	–	–	21.8	21.9	21.5	20.9	–	–
Mesamoll blend	–	–	15.1	14.0	15.2	15.8	–	–
Lindol control	33.4	32.4	31.2	30.2	29.3	30.2	–	–
Lindol blend	27.8	28.6	27.5	27.7	29.0	29.1	–	–
2–45 control	24.3	23.9	23.4	23.3	22.6	23.0	21.3	–
2–45 blend	21.2	22.6	22.2	22.2	23.2	23.0	21.3	–

heterogeneous systems given that such systems facilitate penetration of moisture and growth of fungi in the interfacial regions [17, 21].

Formulation IIA: the fungal growth rating is the same as was found for Formulation II (i.e. 0), with similar weight loss. However, the modulus, yield and break strength are lower than was found in Formulation II. Together, these data indicate a certain efficiency of the biocide. A result that was not expected was the increase in elongation at break that is the same level as reported in Formulation I.

DOP in blends

Formulation I: this formulation was found to have a fungal growth rating of 3, weight loss higher than that of the respective control, a slight increase in T_g, with elongation slightly decreased but, surprisingly, the modulus and strength at yield and break decreased as well. The reason for the decreases in modulus and strength may arise from an attack by fungi on the AL. Lignin macromolecules are very complex and have a tendency for association, which makes them usually very resistant to biodegradation. Studies undertaken in our laboratory have demonstrated that it is possible to decrease the degree of L's association through the use of specific plasticizers [10]. DOP only partly plasticizes AL and consequently only small quantities of L's low molecular weight fractions are free to interact with polar VC-VAc polymer. This typically would result in the formation of H-bonds between OH groups of the AL and α-hydrogen present on VC units or carbonyl groups of VAc units. If the AL's low molecular fractions are partially destroyed by specific enzymes or acids produced by fungi, some of the secondary bonding between AL and the copolymer will vanish, and in turn the strength of the polymer matrix will be reduced.

Formulation IA: as was found for Formulation I, this formulation exhibits a decrease in fungal growth with similar changes in mechanical properties, although to a lesser degree. As in DOP control Formulation IA the slight deterioration of the material suggests that there is either an insufficient concentration of biocide in the formulation or that the biocidal agent is unable to adequately diffuse from and migrate to the surface of the material.

Formulation II and IIA: both the SS and IS specimens of the blends obtained with these formulations are very stiff as characterized by high strength at break and low elongation in comparison with the respective blends obtained with Formulations I and IA. The difference between the T_g of SS control and T_g of SS blend is around 4°C whereas in Formulation I, the difference is about 10°C. The reason for the high degree of stiffness of these specimens is not immediately clear, although the presence of paraffin wax (totally non-polar lubricant) may prevent the adequate dispersion of the AL through the polymer matrix. The stiffness of the blends and their T_g suggest a higher degree of association within the AL components. Li et al. reported that the tensile behavior of L-based blends is directly dependent on the degree of association between the L macromolecules. The higher the degree of association among L components, the higher is the blend stiffness [22]. If the morphology of these blends is different than that of those obtained with Formulation I, the fungal attack will likewise be different. If one compares the intensity of microorganism's growth in Formulations I and IIA, one may notice sensible differences, from medium growth (30–60% of the surface) to none respectively. Consider as well that the changes in mechanical properties brought about by the effects of fungal deterioration are very similar. Based on these observations one may conclude that the changes in mechanical properties are not in agreement with the intensity of fungal growth. Other authors have made the same observation [18].

Mesamoll in controls

The changes in mechanical properties and T_gs, as well as weight losses of all the controls specimens, due to the effects of biodeterioration, compare well with the changes observed in similar formulations plasticized by DOP. The only exception is the Formulation IIA in which the modulus and tensile strength decrease and elongation increases. The material obtained with this formulation seems to be more plasticized. The effect of plasticization may be attributed to traces of water still present into the formulation at the time of testing. It was shown that presence of bound water molecules could disrupt the interaction between vinyl polymer chains, bringing about further plasticization [23].

Mesamoll in blends

In general, the susceptibility of these blends to microorganisms attack is comparable to that of DOP plasticized blends. It is interesting to note that the loss in weight evident in Formulation IA specimens, for which the fungal rating was 1, is slightly higher than that of Formulation I specimens having a fungal rating of 3. The results of an international cooperative experiment, described in reference [24], on the biodegradation of plasticized PVC films by a mixture of six fungi (four of which are similar to those prescribed in ASTM G21 with *Chaetomium globosum* replaced by *Aspergillus versicolor* ATCC #22730 and *Pullularia pullulants* ATCC #9348), have indicated that the weight losses are related to the degradation of the plasticizer in the film. Plasticizer loss, however, was greater than the weight loss as it was confirmed by a precise and reproducible extraction method. This discrepancy was explained by the fact that apparently, the biodegradable component of the plastic formulation is only partly broken down. Non-extractable metabolic residues must remain within the plastic film. Although the author did not negate the value of the weight loss data, he indicated that caution is necessary in interpreting these data.

As the biodegradable components of the abovementioned blends are probably plasticizer, additives and AL, it may be possible that in some instances, metabolic residues of partially broken down AL have greater chances to remain within the material.

Lindol in controls

Formulation I: the trend in changes of mechanical properties after the incubation period is similar to control samples plasticized with DOP. However, the weight loss is

Table 11 Fungal growth rating, ΔT_g, % loss in weight and % changes in mechanical properties of IS versus SS for control and blend specimens after 28-day incubation period

	DOP		Mesamoll		Lindol		2–45	
	Control	Blend	Control	Blend	Control	Blend	Control	Blend
Formulation I								
Fungi rating	1	3	1	3	1	1	2	4
ΔT_g (°C)	−1.2	2.1	n.a.	1.9	−1.0	0.8	−0.4	1.4
Loss in weight	0.119	0.197	0.128	0.204	0.075	0.200	0.298	0.584
Modulus	8.4	−11	n.a.	n.a.	6.0	5.8	4.5	13.2
Yield strength	3.8	−10.1	n.a.	n.a.	0.8	0.8	6.5	14.8
Break strength	3.6	−1.7	n.a.	n.a.	5.8	0.9	0.2	4.5
Elongation	4.4	−1.4	n.a.	n.a.	29.5	−13.5	−1.5	−3.3
Formulation IA								
Fungi rating	0	1	0	1	0	0	1	0
ΔT_g (°C)	0.9	0.3	0.1	0.3	−1.0	0.2	−0.1	0
Loss in weight	0.103	0.186	0.094	0.211	0.035	0.163	0.208	0.440
Modulus	7.2	−4.8	2.8	4.5	8.0	3.4	2.7	2.9
Yield strength	1.1	−0.8	0.2	2.2	3.8	−3.8	2.8	6.9
Break strength	6.1	1.8	0.6	0.2	4.8	−2.1	6.0	–
Elongation	−4.5	−5.6	−4.3	−8.6	−3.3	15.6	−2.1	−4.1
Formulation II								
Fungi rating	0	3	0	3	0	2	1	4
ΔT_g (°C)	2.2	0.2	2.2	0.6	0.9	0.1	0.4	−1.7
Loss in weight	0.093	0.197	0.096	0.170	0.130	0.198	0.302	0.790
Modulus	20.3	2.0	17.8	−4.6	11.3	6.0	30.0	14.9
Yield strength	7.2	–	2.7	–	11.6	–	5.2	6.1
Break strength	2.5	5.8	0.2	2.1	9.0	1.3	0.2	−6.2
Elongation	−8.2	*	−13.4	*	9.2	*	−18.8	−24.4
Formulation IIA								
Fungi rating	0	0	0	0	0	0	0	2
ΔT_g (°C)	n.a	n.a.	n.a.	n.a.	n.a.	n.a.	n.a	n.a
Loss in weight	0.093	0.155	0.085	0.168	0.128	0.148	0.286	0.609
Modulus	6.5	−11.1	−4.0	−4.1	9.1	−6.9	14.3	−13.7
Yield strength	4.8	–	−2.6	–	−24.1	–	0.9	−8.1
Break strength	2.8	−2.6	−1.2	−1.9	17.1	−3.7	0	2.3
Elongation	33.2	*	12.2	*	−18.4	*	−7.4	13.4

*The elongation values of both SC and IS are too small to obtain significant results from their differences the smallest of all the controls obtained with this formulation. Bearing in mind the earlier observation regarding the interpretation of data in respect to loss in weight is difficult to discern if the weight loss reflects a better resistance of this plasticizer to fungal attack in comparison to the other plasticizers. As in the case of DOP plasticized blend, the elongation at break had unexpectedly increased.

Formulation IA: the fungal growth rating and the weight loss confirm the efficiency of the biocide, but a comparison of the changes in mechanical properties with those observed in Formulation I do not confirm the efficiency of the biocide. The same observation is applicable if one compares changes of mechanical properties between Formulation II and IIA. One may conclude again (see DOP in Blends) that changes in mechanical properties as effect of fungal attack are not in agreement with fungal growth rating and weight loss values.

Lindol in blends

Formulation I: for this formulation the increase in the T_g, weight loss, and fungal growth rating are the lowest values obtained of all the blends having the same formulation. In contrast to the blends plasticized with DOP, in this Lindol plasticized blend the T_g increased to a lesser extent and the modulus, strength at yield and break increased and elongation decreased. Such results rather reflect a loss of plasticizer compared to a loss in AL, which is indicative of the distinctive biodegradation mechanism of this blend.

Formulation IA: there was not visible fungal growth on the surface of this specimen and the weight loss was the lowest in comparison to the other blends obtained with this formulation. Presumably its distinctive morphology impedes to a great degree the fungal attack without completely preventing it. The changes in mechanical properties (except a slight increase in modulus) are likely due to additional plasticization by traces of still present water, as was observed and discussed in the case of the control specimens plasticized by Mesamol in Formulation IIA.

Formulation II and IIA: these blends are very stiff and similar to those plasticized with DOP and Mesamoll. In general, the changes in the mechanical properties and weight losses, due to biodeterioration, are also similar to those plasticized with DOP and Mesamoll where the fungal growth rating is 3, whereas the fungal growth rating is 2 in Formulation II plasticized with Lindol.

2–45 in controls

Formulation I and IA: from all the controls obtained with Formulation I and IA those plasticized with 2–45 exhibit the highest degree of fungal growth rating (values of 2 and 1 for Formulations I and IA respectively), the highest loss in weight and the lowest decrease in the T_g. In addition, there is a modulus increase, an elongation decrease as well as an increase of yield and break strength that agree quite well with fungal growth rating and weight loss. This indicates without doubt a loss of plasticizer and additives content in both formulations. As was the case for the other formulations, the biocide to a certain degree helped in reduce microorganisms's growth without completely inhibiting their development.

Formulation II and IIA: data presented in Table 11 indicate that all the control specimens of Formulation II do not have traces of fungal growth on their respective surfaces, although the changes in mechanical properties as well as weight loss, suggest a loss in plasticizer due to the effects of biodegradation. Only on the control specimens plasticized with 2–45 were, traces of fungal growth easily detected, and additionally, weight losses and changes in mechanical properties indicate a higher loss in plasticizer than in the other controls.

2–45 in blends

Formulation I: after 28 days incubation there was a massive growth of sporing fungi on surfaces of blend specimens (>60%) associated with strong discoloration, substantial changes in mechanical properties as well as the highest weight loss among all the different blends. This collective data demonstrates that both the plasticizer and AL suffer serious changes due to the effects of fungal attack. Most likely, these results are brought about by the high degree of 2–45 plasticization of the AL.

Formulation IA: properties of this formulation (Table 11) show no fungal growth (0), accompanied by a substantial weight loss; this formulation represents a typical example of the fact, discussed earlier, that although the fungal growth on a specimen surface is not visible, biodeterioration can nonetheless occur.

Formulation II and IIA: as can be seen from the results given in Tables 6–10, in contrast with the other blends prepared with these formulations, the 2–45 plasticized blends are tougher, as is characterized by higher values of modulus and yield strength and high elongation at break. Surprisingly paraffin wax lubricant did not impede, as it did in the presence of other plasticizers, the dispersion of AL within the polymer matrix.

The specific observations that can be drawn from the analysis of the above results are:

1. Based on a visual examination of the control specimens, the susceptibility to fungal growth of formulations plasticized with DOP, Mesamoll and Lindol are similar in Formulation I (less than 10 % of the surface covered by fungal growth) and that of the formulation

plasticized with 2–45 slightly greater (10–30% of the surface). Based on weight loss, the resistance of the different plasticizers to fungal growth can be rated in order of: $\mathrm{Lindol} > \mathrm{DOP} \geq \mathrm{Mesamol} > 2-45$. However the degree of fungal growth and weight loss did not correspond with changes in mechanical properties.

2. In Formulation II no fungal growth was detected on the surfaces of control specimens plasticized with DOP, Mesamoll and Lindol and only traces (less than 10%) were observed on the surfaces of specimens plasticized with 2–45. It is obvious that the heat stabilizer and lubricant utilized in Formulation I represented an easy nutrient source for the fungi. The order of weight loss gave the same plasticizer rating as in Formulation I, and changes in mechanical properties did not correspond with the fungal growth or weight losses.
3. The biocide provided a certain protection against fungi, as can be seen from the decrease in fungal rating on all the specimens formulated with it. However, the weight losses as well as changes in mechanical properties and T_g indicated that the protection was incomplete as long as certain deterioration still occurred within these formulations that incorporated a biocide. Initially it was believed that the deterioration was due to an insufficient concentration of biocide and/or its ability to diffuse out of the material. The concentration of the biocide corresponded to the value indicated by the producer. On further reflection, it was possible to suggest a possible reason for its inability to protect the materials. During the incubation period under the effect of time and temperature a physical aging will occur in all materials. Data taken from the literature [25, 26] indicate that if the aging temperature is below the T_g of plasticized PVC, an improved structural ordering will occur in the amorphous phase. It is seen to result from the relaxation of the polymer chains, eliminating the excess free volume, in an effort to approach the preferred or true equilibrium state of the system. This behaviour is manifested, among other phenomena, through a slow decrease in volume (densification). An aging temperature above the T_g of plasticized PVC causes formation of small crystallites in the polymer system, that allow the formation of a three dimensional network, in which entanglements and small crystallites act as junction points or physical cross-links of the structure. Thus, the main consequence of these two phenomena is that the polymer matrix becomes more compact. Not only the mechanical properties, but also the transport phenomena of liquid and vapors in or out of PVC samples are strongly dependent of free volume variations and/or the presence of crystallites [26]. As result, this compact structure prevented the desorption of water, thus increasing the necessary drying period. Also, a more compact structure may encapsulate the biocide, thereby hindering its migration to the surface where biodeterioration mainly takes place. Information from literature confirms this possible mechanism [27].
4. The fungi have shown a stronger ability to degrade the blends as compared to the control formulations. In comparison with the respective controls the blend specimens exhibited higher fungal growth rates or, at similar rates of fungal growth, higher weight loss. Our previous data had shown that this particular fungi mixture does not affect AL alone. Visual and microscopic examination did not detect fungal growth on the inoculated AL samples after the same incubation period, an observation that was also confirmed by results obtained by FTIR spectroscopy, for which, no changes in spectra were evident [28]. So it is clear that the AL attack occurred, differently, in the presence of specific plasticizers when the degree of association between L's macromolecules is decreased. Dissociated AL's structures having smaller molecular weights than the average MW of AL can be easily broken down and assimilated by microorganisms. The blends formulated with 2–45 plasticizer, which is most effective plasticizer for AL from all the four tested, displayed the highest degree of deterioration. It is interesting to note that Lindol too is a good plasticizer for AL. However in comparison with the blends plasticized by DOP and Mesamoll most of the Lindol plasticized blends are the less susceptible to fungi attack.

After the fungal attack most of the blends, which initially all were dark brown, presented a certain degree of discoloration, the greatest belonging to 2–45 plasticized blends and the lowest to Lindol plasticized blends. α- carbonyl structures conjugated with aromatic double bonds and phenolic hydroxy groups, are the principal chromophoric groups in L. It was demonstrated that phenoxy radicals are the intermediates in the degradation and discoloration processes of L. The phenoxy radicals are formed as effect of UV light, mainly from the aryl-α-carbonyl structures and structures containing double bonds in conjunction with aromatic rings, either by a direct hydrogen abstraction mechanism, from free phenolic units, or by generation of singlet oxygen which is able to create phenoxy radicals [29–31].

It could be possible that the various types of acids produced by the fungi were able to break these structures or part of them, and consequently induce discoloration of the AL.

Conclusion

1. New vinyl flooring formulations where 20 parts of vinyl polymer was replaced with an organosolv lignin were prepared and tested for their resistance to fungal attack using an ASTM test method for determining the resistance of plastics to fungal growth. The research sought to develop materials with higher resistance to fungal attack, and consequently with a low long-term emission of VOC.
2. As information in literature has indicated all the results of this testing method should be interpreted with caution because each particular formulation has its specific chemical composition and consequently each microorganism-formulation couple has unique degradation kinetics, that are difficult to interpret based solely on the types of tests undertaken in this study. Further investigation would probably allow better identification of such observations.
3. Although each plasticizer has a specific resistance to hydrolysis due to differences among ester groups, the visible effects of fungal attack, in formulations without AL, is similar for all plasticized controls, with the exception of formulations incorporating diethyleneglycol dibenzoate, in which a higher degree of biodegradation was always present. Based on the weight loss of specimens formulated without AL, their resistance to fungal attack can be rated as follows: $\text{Lindol} > \text{Mesamoll} \geq \text{DOP} > 2-45$. The same rating is applicable for blend specimens.
4. The presence of fatty acids derivatives utilized as additives (i.e. as heat stabilizer and lubricant) render the materials less resistant to attack by fungi.
5. A certain amount of biocide is able to provide an enhanced resistance to biodegradation to all formulations evaluated in this study.
6. The results demonstrated that each particular AL-plasticizer-additives formulation has its specific mechanism of biodegradation.
7. Formulations, where AL replaced 20 parts vinyl polymer, plasticized with Lindol and formulated with biocide have the same resistance to fungal attack as similar controls plasticized with DOP, Mesamoll and Lindol and where the vinyl resin is the sole polymer.

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