STUDIES ON THE MISCIBILITY OF POLYVINYL ALCOHOL AND NITROCELLULOSE BLENDS FOR WOOD-COATING

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ABSTRACT

Polyvinyl alcohol (PVA) was prepared from polyvinyl acetate by suspension polymerization method and blended with Nitrocellulose (NC), degree of substitution 2.26 at different ratios of the polymer components in the blend solutions. The blends of PVA: NC were prepared by solution casting method. The blend films obtained were characterized by FTIR, DSC, and SEM techniques and the results were used to investigate the miscibility of these blends. The results revealed that the blends were miscible in most of the ratios except for PVA 60:NC40 which was manifested in the DSC as well as the SEM micrograph. Finally, the blends were applied on wood surfaces with satisfactory results such as good adhesion to the surface of the wood, glossiness and transparency. They were subsequently compared to the existing wood-coating materials in the local market. The blends showed some resemblance with the existing wood-coating materials in some cases while blends (PVA: NC) 10:90 and 20:80 showed better shining properties.

Keywords: Blends, Miscibility, Nitrocellulose, Polyvinyl alcohol.

INTRODUCTION

Polymers play important role in industries today and there is a huge resurgence of interest in developing new polymeric materials via the combination of existing commercially proven polymers [1]. This trend is expected to continue into the foreseeable future for several reasons, among which are economic stresses, technological constraint, government regulatory edicts, to dilute high-cost engineering resins with low-cost polymers, to form high performance blends from synergistically interacting polymers, to adjust composition to suit customers, to recycle industrial plastic scraps, the necessity to conserve the world's dwindling resources and to encourage green chemistry. This work focuses on the study of polymer

blends from polyvinyl alcohol and Nitrocellulose and their application on wood. Polyvinyl alcohol has outstanding properties found to be useful in so many areas of life, but its rigidity [2] and poor flexing endurance [3] result to its limitations in some cases. Adding a more flexible and elastic polymer like nitrocellulose would create a hybrid polymer with better properties.

The aim of this research work is to prepare blends of fully hydrolysed polyvinyl alcohol and nitrocellulose and to investigate the effect of the miscibility on individual properties and coating on wood.

Objectives

i. To prepare poly (vinyl acetate) from a purified vinyl acetate monomer.

ii. To prepare a fully hydrolysed PVA by hydrolysis of the poly vinyl acetate.

iii. To blend the PVA with nitrocellulose at varying ratios.

iv. To characterize the PVAc, PVA, NC and PVA/NC blends using FTIR, DSC, SEM, and viscometry analysis and coating the polymer lends on wood.

MATERIALS AND METHODS

Vinyl acetate monomer (CDH), Carboxy methyl Cellulose (CMC) (Akay Organics), N-hexane (BDH), Aluminium peroxide(Core Bit. U$^-$Bolt), Benzoyl peroxide (BPO) (JobinChemical Pvt. Ltd), Distilled water, H_2SO_4 (JHD), NaOH (JHD) , acetone, ethanol, nitrogen gas. Polyvinyl alcohol, Nitrocellulose (Sigma).

Equipment

In addition to common laboratory wares, Ostwald viscometer, FT-IR machine (Cary-630, Agilent technology at frequency range 4000-650cm^{-1}) Soxhlet extractor, Liebig condenser, Leica Stereoscan-440 scanning electron microscope equipped with phoenix EDX Attachment. Magnification:-1000x-100x, DSC II STAR SW 13.00 SYSTEM METTLER and water bath (H H-4, KW1000DC).

Preparation of Benzoyl peroxide crystals

BPO (5g/0.02 moles) was dissolved in ethanol with little warming on magnetic stirrer until the BPO dissolved completely. The solution was poured unto funnel with filter paper while the conical flask was placed in ice block. The solution was filtered to obtain a pure and shining BPO crystal. The crystals were subsequently desiccated for three days [4].

Vinyl acetate monomer

To remove the inhibitor in the monomer, the vinyl acetate monomer was purified by passing it through a column of aluminium oxide. The filtrate was collected in an enclosed dark bottle (to prevent polymerization by interaction with light) at a reduced temperature using water bath [4].

Nitrogen gas

The gas was purified by passing it through pyrogallol, distilled water, conc. Sulphuric acid, phosphorus pentoxide in succession.

Synthesis of Polyvinyl Acetate

Carboxy Methyl Cellulose (0.166g/ 0.00069 moles) suspension agent was dissolved in 90ml of distilled water under nitrogen atmosphere and constantly stirred in three-neck round bottom flask fitted with stop cock [4].

Subsequently, Vinyl acetate monomer (50ml) and Benzoyl peroxide (0.5g/0.002 moles) were added at once, at a fixed temperature of 60°C, the reaction mixture was stirred for 2h. The polyvinyl acetate was filtered and washed with warm water to remove the residual suspension agent, and then purified in N-hexane to remove unreacted monomer [4]
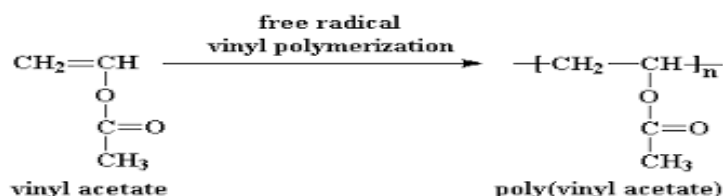

Figure 1: Polymerization of vinyl acetate to polyvinyl acetate.

Hydrolysis of Polyvinyl Acetate

Polyvinyl acetate (10g/0.116 moles) was added to Methanol (125ml) containing Sodium hydroxide solution (1.25ml 40%) and was heated under reflux for 30 minutes. The solid was separated by filtration, transferred to a Soxhlet and extracted overnight with methanol at 57°C. The extract solid was allowed to air dry at room temperature [4].
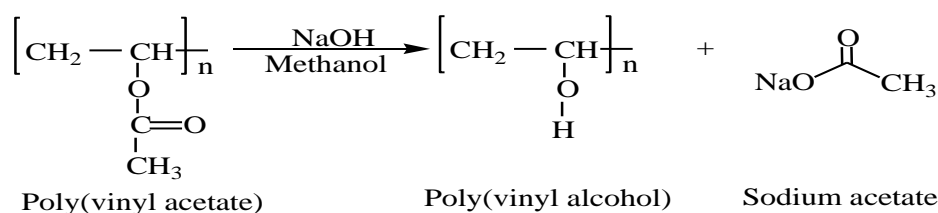

Figure 2: Hydrolysis of polyvinyl acetate to polyvinyl alcohol.

Preparation of films of PVA, NC and their blends

Solution of polyvinyl alcohol (5%) in water while Nitrocellulose was mixed with water in the ratio 3:2 i.e. NC (3g/0.003moles) water (2g/0.111 moles). They were all prepared separately. The films were cast from these solutions separately and in blends. The films were subsequently cast on glass plates by dropping 10ml of solutions with pipette and spread evenly using a Doctor's blade with a gap of 400-450μm to generate a film thickness of 122-150 μm. The spread solutions were allowed to dry in the surrounding environment to form a uniform thickness on the glass. After seven days, the film coated glasses were quenched in water so as to disengage the film from the glass. The separated films were finally air dried at 25ºC [3].

Film characterization

The films produced were characterized by Fourier- Transform Infrared (FT-IR) spectroscopy, Differential Scanning Calorimetry (DSC) and Scanning Electron Micrography (SEM) to ascertain their constitution and assess their physical, thermal and chemical properties.

FT-IR analysis

The samples were subsequently analysed using a Fourier-Transformer Infra-Red (FT-IR) spectrometer (Cary 630, Agilent technology, USA) model frequency range, 4000-650cm^{-1}. All the spectra were recorded over the range of 4000-650cm^{-1}

Scanning Electron Microscopy

Scanning Electron Microscopy was used to investigate the miscibility and roughness of the polymers i.e. from monomer to polymer to polymer blends through morphology analysis [4]. The instrument used was Leica Stereoscan-440 Scanning Electron Microscope (UK) equipped with phoenix EDX Attachment. Magnification:-1000x-100x.

Differential Scanning Calorimetry

Differential Scanning Calorimetry measures the amount of heat that a sample absorbs or releases as a function of temperature and time, when it undergoes certain phase transition/transformation, and/or reactions. Essentially, a temperature program is applied to a sample and a reference material and the difference in the amount of heat flux is recorded that is required to maintain both sample and reference at the same temperature [4]. The instrument used was DSC II STAR SW 13.00 SYSTEM METTLER (UK), temperature range from 300-60˚C. At the heating rate of 10°C/min.

Viscosity measurement of PVAc

Relative viscosity of the prepared PVAc was measured at different concentrations in acetone, using Ostwald viscometer at 25°C room temperature.

This was achieved by dissolving 1.0 g, 0.8 g, 0.6 g, 0.4 g and 0.2 g of PVAc in 100 ml acetone each. The flow time of the pure solvent (acetone) was recorded in seconds as (t_o) and the flow time of dilute polymer solution was also measured and recorded in seconds as (t).The relative, specific and reduced viscosity were all calculated using eq.8, 9 and 10 respectively while the intrinsic viscosity was eventually determined through extrapolation from the graph [5]. The same procedure was taken for Viscosity Measurement of PVA in water at 80°C using water bath to maintain the temperature.

RESULTS AND DISCUSSION

Percentage yield of PVAc and PVA

Table 1: % yield of polyvinyl acetate and polyvinyl alcohol

Polymer	% Yield
PVAc	50.40
PVA	35.00

The percentage yield was determined using eq.1

$$\% \, Yield = \left(\frac{w_1}{w_2}\right) \times 100$$

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Where W_1 = mass of monomer

W_2 = mass of polymer obtained from the monomer.

FT-IR Results

Table 2: FT-IR absorption frequencies (cm^{-1}) of Vinyl acetate and polyvinyl acetate

GROUPS	Vinyl acetate	Poly Vinyl acetate
CH	3095	2969
C=O	1758	1732
C-O	1208	1225
C=C	1648	-
CH	1372	1372

Table 3: FT-IR absorption frequencies (cm^{-1}) of PVA, NC and their blends at different ratios

GROUP	PVA 100%	NC100%	PVA80/NC20	PVA60/NC40
OH	3430	3427	3383	3390
CH	2933	2929	2929	2929
C-O	1015	1030	1030	1030
O-N=O	-	1644	1644	1644
C-NO$_2$	-	1279	1279	1279

Table 4:   FT-IR absorption frequencies of blends.

GROUPS	PVA50/NC50	PVA40/NC60	PVA20/NC80	PVA10/NC90
OH	3373	3368	3372	3410
CH	2929	2929	2929	2933
C-O	1030	1030	1037	1030
O-N=O	1644	1644	1644	1648
C-NO$_2$	1279	1279	1279	1279

Features of films.

Table 5: Features of Films from PVA, NC and their blends.

Samples	flexibility	texture	transparency	elasticity
100% PVA	slightly flexible	slightly rough	transparent	slightly elastic
100% NC	very flexible	very smooth	transparent	elastic
PVA 80/NC20	flexible	slightly smooth	transparent	slightly elastic
PVA 60/NC40	flexible	smooth	transparent	elastic
PVA 50/NC50	flexible	smooth	transparent	elastic
PVA 40/NC60	flexible	smooth	transparent elastic	
PVA 20NC80	very flexible	very smooth	transparent	elastic
PVA 10NC90	very flexible	very smooth	transparent	elastic

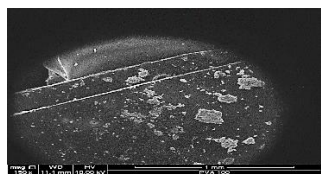## Scanning Electron Microscopy

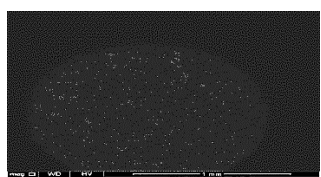Figure 3: The SEM micrograph of 100% polyvinyl alcohol

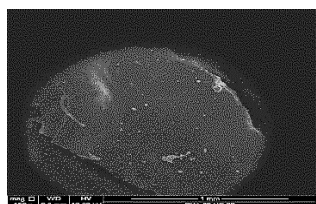Figure 4: The SEM micrograph of 100% Nitrocellulose

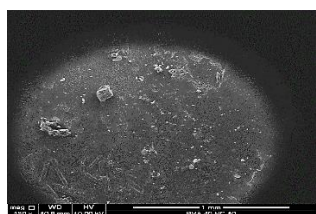Figure 5: The SEM micrograph of 80:20 (PVA: NC) blend

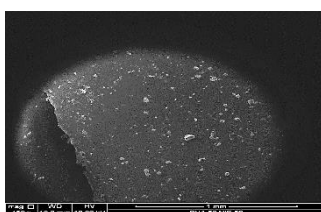Figure 6.The SEM micrograph of 60:40 (PVA: NC) blend.

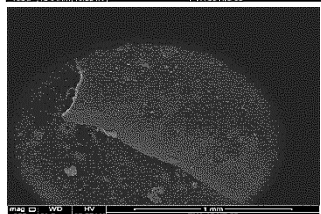Figure 7: The SEM micrograph of 50:50 (PVA: NC) blend

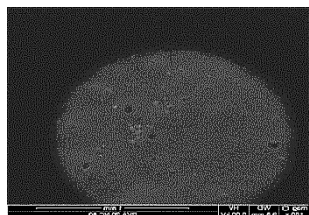Figure 8: The SEM micrograph 40:60 (PVA: NC) blend

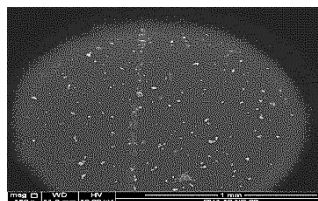Figure 9: The SEM micrograph of 20:80 (PVA:NC) blend

Figure 10: The SEM micrograph of 10:90 (PVA:NC) blend

Table 6: DSC parameters of PVA, NC and their blends at different ratios.

	Polymers	Tg	Tc	Peak type
1	PVA 100%	94.32	128.08	Exothermic
2	NC 100%	84.7	119.91	Exothermic
3	PVA80:NC20	93.47	106.74	Exothermic
4	PVA60:NC40	88.67/167.19/243.50	105.09/173.16/273.17	Exothermic
5	PVA50:NC50	94.37	113.62	Exothermic
6	PVA40:NC60	85.72	92.83	Exothermic
7	PVA20:NC80	86.98	91.66	Exothermic
8	PVA10:NC90	81	92.17	Exothermic

Viscometry

Table 7: The intrinsic viscosities and average molecular weights of PVAc and PVA.

Polymer Intrinsic viscosity (dL/g)		Average molecular weight(g/mol)
PVAc	0.54	84,000
PVA	0.17	11,000

The average molecular weights were determined through Mark Houwink equation [n]= KM^a_w. For polyvinyl acetate, the Mark Houwink's constants (a=0.680; K=0.000214dl/g) in Acetone at $25°C$. For polyvinyl alcohol, the Mark Houwink's constants (a=0.5600; K=0.0009400) in water at $80°C$.

Dilute solutions of polymers were prepared as earlier discussed in acetone and water for PVAc and PVA respectively. The viscosities of the polymers were measured using Ostwald viscometer at their corresponding temperatures. The intrinsic viscosity was calculated using Mark Houwink equation. Subsequently the equation was used to determine the average molecular weight of polymers. $[\eta] = KM^a$

Where = K and a are Mark Houwink constants.

M = molecular weight of polymer.   [n] = Intrinsic viscosity

Table 8: Comparison between the PVA, NC, blends and some wood-coating materials

COATING MATERIAL	APPEARANCE	ADHESION	CURING	REVERSABILITY
Super varnish	Glossy, transparent, smooth and golden yellow	Good	Slow curing	Non reversible using water and ethanol
Glossy Lacquer	Moderately glossy, transparent and smooth	Good	Very fast curing	Non reversible using water and ethanol
Spies varnish	Very glossy, transparent, smooth and golden yellow	good	Slow curing	Non reversible using water and ethanol
100% Nitrocellulose	Glossy, transparent and smooth	Good	Moderate curing	Reversible using water and ethanol
100% Poly (vinyl alcohol)	Glossy, transparent and slightly rough	Good	Fast curing	Reversible using water and ethanol

Table 9: Features of blends on woods

COATING MATERIAL	APPEARANCE	ADHESION	CURING	REVERSABILITY
PVA80/NC20	Glossy , moderately transparent and smooth	Good	Moderate curing	Reversible using water and ethanol
PVA60/NC40	Very glossy, moderately transparent and smooth	Good	Moderate curing	Reversible using water and ethanol
PVA50/NC50	Very glossy, moderately transparent and smooth	Good	Moderate curing	Reversible using water and ethanol
PVA40/NC60	Poorly glossy, transparent and smooth.	Good	Moderate curing	Reversible using water and ethanol
PVA20/NC80	Very glossy, transparent and smooth	Good	Moderate curing	Reversible using water and ethanol
PVA10/NC90	Very glossy, transparent and smooth	Good	Moderate curing	Reversible using water and ethanol

Percentage yield of PVAc and PVA

From Table 1, the yield of the polyvinyl acetate obtained from the polymerization of vinyl acetate was 50.40%. This was due to the increase in polymerization time [4]. While the percentage yield for the PVA obtained was 35%.

Viscosity

Viscosity measurement was carried out using Ostwald viscometer to determine the intrinsic viscosity of the polymers consequently obtaining the viscosity average molecular weight of the polymers. From Table 7, average molecular weights obtained for both PVAc and PVA were 84,000 g/mol and 11,000 g/mol respectively, while their intrinsic viscosities were approximately 0.54 dL/g and 0.17dL/g for PVAc and PVA respectively.

FT-IR of PVA, NC and their Blends.

FT-IR spectroscopy has been widely used by many researchers to study the formation of blends. FT-IR provides information regarding intermolecular interactions via analysis of FT-IR spectra corresponding to stretching or bending vibration of particular bands and positions at which these peaks appear depending directly on force and band strength. Hydrogen bonding or other

secondary interactions between groups on the dissimilar polymers should theoretically cause a shift in peak position of the participating groups [2]. This kind of behaviour is exhibited by miscible blends that show extensive phase mixing. Hydrogen bonding interactions usually move the stretching frequencies of participating groups e.g O-H towards lower numbers usually with intensity and peak broadening. The shift in peak position will depend on the interaction between the compositions [6]. From Table 2, in the vinyl acetate spectrum there are important vibrations identified as C-H 3095 cm^{-1} stretching, carbonyl C=O 1758 cm^{-1}, C-O 1208 cm^{-1}, C=C 1648 cm^{-1}. For the polyvinyl acetate there is disappearance of C=C, C=O at 1732 cm^{-1}, C-O at 1225 cm^{-1} and C-H 2969 cm^{-1}. According to Table 3, in the spectra film of PVA, one of the most prominent features is the –O-H stretching vibration at 3430cm^{-1}. Others are C-H 2933 cm^{-1} and C-O stretching at 1015cm^{-1} as reported by Gumel and Danbatta [3]. In the NC spectra, there is an –O-H stretching vibration peak at 3427 cm^{-1} stretching which corresponds to intermolecular hydrogen bonding, which is due to residual –O-H group present in the polymer based on the degree of nitration 2.26 [4]. Other vibrations of NC are C-O 1030cm^{-1}, O-N=O1644cm^{-1}, C-NO$_2$ 1279 cm^{-1}. The PVA peak is clearly distinguished from the NC peak due to the high degree of -O-H while the low peak of NC peak may be due to high degree of substitution of H by Nitro groups. The formation of hydrogen bond between PVA and NC and their blends were demonstrated by FT-IR spectroscopy from the shifts of absorption bands showing hydroxyl stretching vibrations, which were sensitive to the hydrogen bonds formed during blending. It was also observed that there were shift in the vibrations from the pure PVA, NC and their blends an observation explained earlier by Satyamaiah *et al* [6], and reported by Gumel and Danbatta[3]; Roumana and Akilandeswari [7]. The shift in the vibrations for PVA/NC blends 10:90, 20:80, 40:60, 50:50, 60:40 80:20 vibrations were recorded as 3410 cm^{-1}, 3372 cm^{-1}, 3368 cm^{-1}, 3373 cm-1, 3390 cm^{-1} and 3383 cm^{-1}respectively which correspond to intermolecular hydrogen bonding, an observation already made by Gumel and Danbatta [3]. The blend films also showed some vibrations typical of both PVA and NC like C-H, C=O, C-O, O-N=O, C-NO$_2$.

Morphology study of films from PVA, NC and their blends.

The dispersion of the solution cast films of pure PVA, pure NC and PVA:NC blend in the ratio 10:90, 20:80, 40:60, 50:50, 60:40 and 80:20 were examined through SEM. As shown in Figure 3

in the SEM micrograph image of PVA, it appeared rough with single phase which may be due to its high viscosity [3] and Guru *et al* [8]. From Figure 4, the surface morphology of NC was evenly dispersed with some particles and showed single phase. However as the PVA increases in the blend, there is more dispersion of the particles. Based on Figures 5, 7-8, and 10 micrograph images of 80:20, 50:50, 40:60 and 10:90 respectively appeared relatively smooth with the PVA particles well distributed in the blend. While Figure 9 micrograph of 20:80 appeared with pores, Figure 6 micrograph of 60:40 appeared rough with the appearance of boundaries or interface which suggests there is low interaction of the polymers at this ratio, which was also supported by DSC technique.

DSC analysis of films

DSC analysis was carried out to determine the miscibility of the blends under study. From Table 6, the correlation of glass transition and crystallization temperature followed the same trend as the percentage of PVA increased in the blend. The films showed sharp exothermic peaks. Most of the blends showed single Tg peak indicating interaction between the component polymers, hence miscibility was achieved [9]. Blend 60:40 has multiple Tg peaks at 105.55°C, 173.15°C and 273.17°C this is as a result of immiscibility of the blend as explained by Satyamaiah *et al* [9]. Another observation is the glass transition temperature (Tg) of individual polymers and their blends which were recorded from the DSC thermographs, the blends exhibited single Tg which were between the Tg of the component polymers (PVA 94.32°C and NC 84.71°C). An interesting observation was the high value of Tg for (PVA:NC) 50:50 at 94.37 which may be due to two factors namely: Intermolecular forces, because strong intermolecular forces caused higher Tg and stiffness due to high % crystallization in the blends. The lowest Tg is recorded for the blend PVA: NC 10:90 (81°C).

Application of polymer films on wood

The Polyvinyl alcohol, Nitrocellulose and their blends were applied onto the wood surface in order to investigate their physical applications and were subsequently compared to the qualities of existing wood-coating materials at the local market in Kano state, Nigeria.

Appearance of blends on wood

From Table 8, blends (PVA: NC), 60:40, 50:50, 20:80, 10:90 and SipesVarnish are all very glossy. S.K. super varnish (S.K. Chemical Industry, Nigeria), 100% Nitrocellulose, 100% Polyvinyl alcohol, blends (PVA: NC), 90:10 and 80:20 are glossy while Glossy Lacquer (Cresol glossy Lacque, Nigeria) is moderately glossy. Blend (PVA: NC) 40:60 is poorly glossy. As observed, the glossiness of the blends increased as the ratio of the NC increased. Blends (PVA: NC), 40:60, 20:80 and 10:90 are all transparent while blends (PVA: NC), 90:10, 80:20, 60:40 and 50:50 are moderately transparent. Though the blends made a good cover up on the wood, transparency and glossiness were improved with increase in NC ratio.

Adhesion of blends on wood

All the coating materials displayed good adhesion to the wood while they varied in other properties. The coating materials as well as PVA, NC and their blends were observed to spread well on the wood without flaking out after drying. The adhesion is assisted due to the presence of polyphenols and other polymers as constituents of natural wood. These may include cellulose, hemicellulose and lignin [10] as most of these polymers contain multiple numbers of OH group. It may be concluded that their good adhesion is attributed to the presence of OH groups.

CONCLUSION

Polyvinyl alcohol was prepared by suspension polymerization method and blended with Nitrocellulose, at different ratios of the polymer components in the blend solutions. The blends of PVA: NC were prepared by solution casting method.

The miscibility studies of polyvinyl alcohol and nitrocellulose blends were carried out using FT-IR, DSC and SEM. Subsequently the blends were applied on wood surface.

The blends covered the wood very well as they served as good coating materials. The appearances displayed by the blends were encouraging as some of the characteristics are satisfactory and could be compared to the qualities of the existing wood-coating materials. The glossy nature of the blends on the wood improved as the proportion of Nitrocellulose increased. Other quality of the blends is the moderate curing time. Thus it could be concluded that the blends of PVA and NC could replace the usual coating of wood surface with pure PVA or pure NC as the blends tend to display better coating properties.

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