Synthesis and Applications of Antimicrobial and UV Protected Polymeric glass coatings

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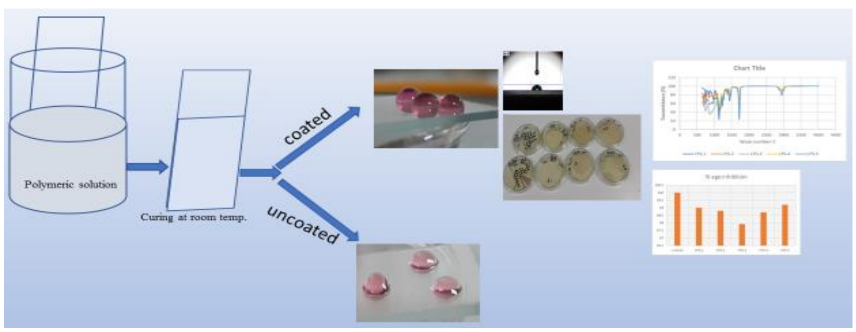
Summary: polymeric materials along with nanoparticles are widely used to protect from microbial propagation. In humid environments, enclosed edifice is amongst the foremost propagation substrates aimed at microorganisms. Antimicrobial coatings could help to stop microbial proliferation or, reduce the number of microorganisms growing on inside buildings. This paper deals with inhibition of *Escherichia coli* bacteria by TiO2 and silver nano-particles doping along with poly acrylate-based copolymers. Coated glass was characterized for FTIR, antimicrobial activity, UV Visible Spectroscopy and water contact angle for hydrophobicity and SEM analysis for surface morphology. The disk diffusion method was used for bacterial inhibition. Results revealed that developed material has good adhesion with glass and shows transparency, hydrophobicity and antibacterial activity. Which shows that coating material can be used for significant antibacterial coatings to protect window glass table ware glass doors etc. further these coatings are transparent, UV radiation protected and hydrophobic in nature which also enhance the self-cleaning effects. In addition, the coating has photocatalytic activity due to the presence of TiO_2 and showed momentous antibacterial events after 2,4 and 6 hrs and this efficiency would be increased by improving formulation composition.



Key Words: Polymeric materials, Antimicrobial, *E. coli*, Self-cleaning, Transparent glass coatings, UV, FTIR, Water-repellent.

Introduction

Antimicrobial, self-cleaning and UV protected coatings are widely used in all field of life. [1-6] Serious hazards cane be caused due to microorganisms producing contaminants, like allergens, pollutants and metabolites [7-15]. Indoor effluence is a solemn communal health issue worldwide. Numerous scientists have previously pointed out that indoor building can be a major put for microbial growth during endorsing ailments, such as highly humid environment. [16]. Sick Structure Syndrome has widespread financial and communal impact [17–19]. Frequent acquaintance to these pollutants can cause numerous health dilemmas, including irritations and lethal effects, infections, aversions and other breathing or skin infections [20]. According to preceding studies exposed that in presence of water photocatalytic process is active against varied organisms, like algae, viruses and bacteria. So developed coating material is hydrophobic and provides no moisture and water for microorganisms to pollute the environment rapidly. Further photo-catalysis of TiO2 also effective to kill microorganisms. Acrylates based coatings also helps in air purification in this regard. [21]. In accumulation to promising claims, self-cleaning coatings also suggested many advantages, plus defence from ecological pollution, removal of repetitive labour-intensive effort, decrease in maintenance costs, and a time saving on cleaning surfaces. [22-23]. Self-cleaning coatings may be hydrophobic and hydrophilic in nature. Both are gifted toClean themselves when water droplets falling upon and roll off dirt particles. Wettability, water contact angle and water sliding angle cane be

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determined by tensiometer. A common example in nature is "lotus effect", where water droplets are hydrophobic on lotus leaf surface. The water contact angles, above 90 degrees refer to as hydrophobic nature [24]. However, the degree of commercial success is still unclear. In addition, TiO_2 can cause photocatalysis due to strong oxidation of organic classes and bacteria on the surface [25]. Antimicrobial coatings are widely used in food packing materials like PPy films on stainless steel via electrochemical deposition technique [26], and polymeric graphite doped sheets by sol gel methods. [27]. Similarly, polymeric SnO2 based packing material along with poly butylene-terephthalate [28]. Such type of coating is helpful for protection against strains and having self cleaning ability so applies successfully on fabrics too [29]

Experimental

Materials

The analytical grade chemicals including Tio2 Nanoparticles, Xylene, styrene, 2-EHA, Butyl Acrylate, Iso butanol, Methyl iso butyl ketone, Methyl Meth Acrylate, Meth Acrylic Acid, Benzoyl peroxide of analytical grade purchased from Sigma Aldrich (Germany). The silver nanoparticles synthesized by using silver nitrate along with lemon leaves extract and imported glass slides purchased from local market.

First copolymer was synthesized doped with0.1% TiO2 and Ag Nanoparticles and then coated on glass substrate after surface activation. Chemical reaction scheme is given below as scheme - 1 and chemical composition is given in Table-1

Method

Homogeneous solution of benzoyl per oxide was obtained by mixing 1.5 grams of initiator in 20 grams of xylene. Added 33 gms. of 2EHA/BA/Styrene along with 100 gms. of MMA.

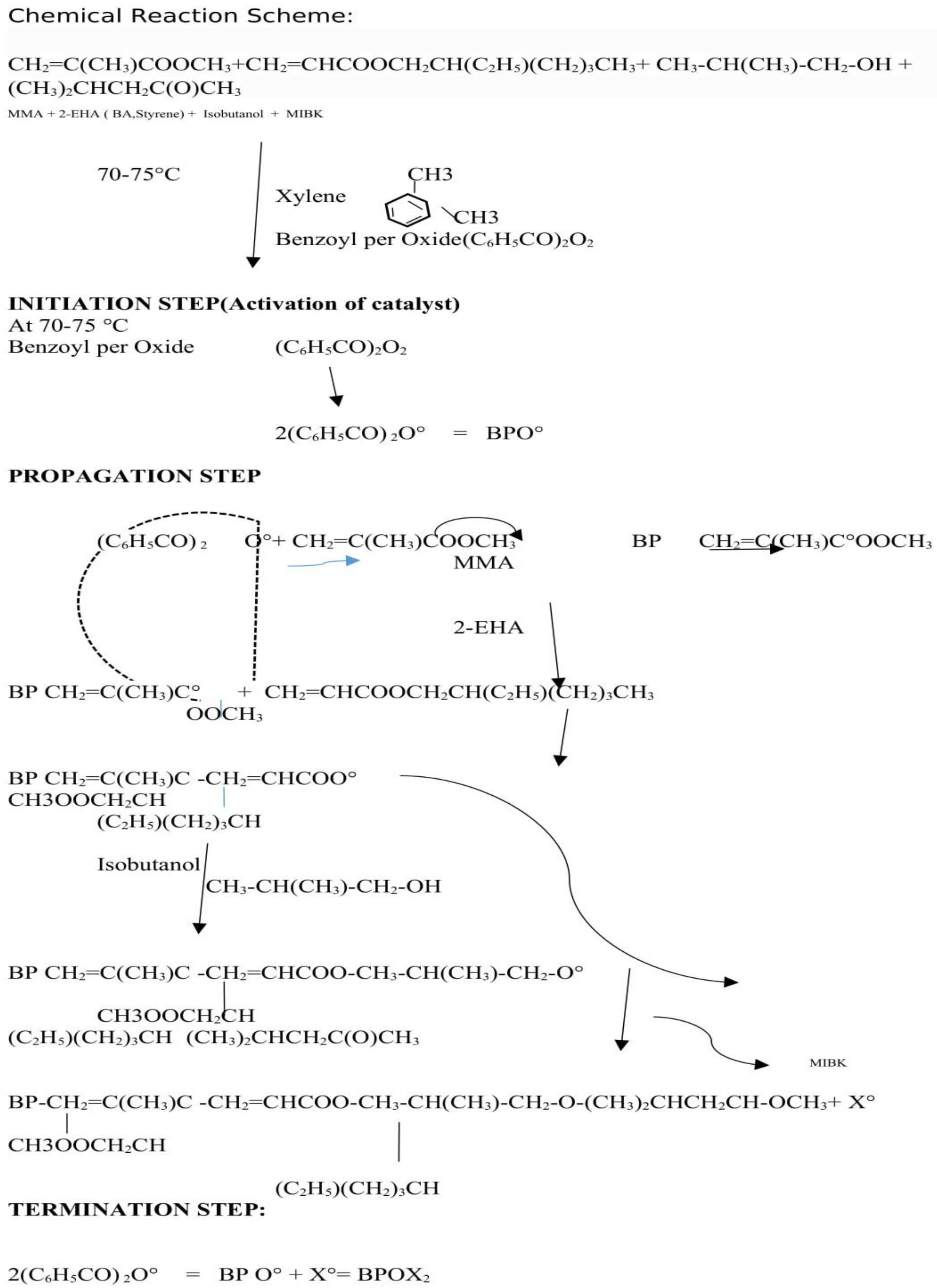
In reaction flask 9 gms of iso butanol ,100 gms. xylene, 3gms. 2EHA and 18.5 gms. of MMA was added and allowed to mix and reflux at 75 to 80 ^{o}C with the addition of initiator solution at five equal intervals. After 3 hrs. digestion completed and stored the product at 45^{o}C.and named as CPS-1, CPS-2, CPS-3, CPS-4 and CPS-5.

Dilution of copolymer, addition of Nanoparticles/ Activation of Glass surface and Coating on Glass

25 Wt /wt % dilution of developed copolymer was made by using solvent. Glass slides of 25 cm* 25 cm was purchased from local market, cleaned and washed with distilled water and surface was activated by using iso-propanol. A 25% diluted copolymer solution in xylene was taken in a beaker then activated Tio2 And Ag nanoparticles 0.025wt% added and stirred for 10 minutes by using magnetic stirrer to get homogenous solution then activated dried glass slide was dipped in this solution for 30-50 second, dried at room temperature for 24 hrs and tested for FTIR, antimicrobial activity, UV-Visible spectroscopy, contact angle, self-cleaning effect and surface morphology via SEM.

Table-1: Composition of Copolymers.

	CPS-1		CPS-2		CPS-3		CPS-4		CPS-5	
Sr #	**Materials**	**% Ratio**	**Materials**	**% Ratio**	**Materials**	**% Ratio**	**Materials**	**% Ratio**	**Materials**	**% Ratio**
1	Xylene	40	Xylene	40	Xylene	40	Xylene	35.6	Xylene	34.5
2	2EthylHexyl Acrylate	12	Butyl Acrylate	12	Butyl Acrylate+ Styrene	12	2-EHA+ Styrene	12	Butyl Acrylate+ Styrene	24
3	Iso butanol	3	Iso butanol	3	Iso butanol	3	Iso butanol	3	Butyl acetate	10
4	Methyl iso butyl ketone	5	Methyl iso butyl ketone	5	Methyl iso butyl ketone	5	Methyl iso butyl ketone	5	Methyl iso butyl ketone	5
5	Methyl Meth Acrylate	39.5	Methyl Meth Acrylate	39.5	Methyl Meth Acrylate	39.5	Methyl Meth Acrylate	39.5	Methyl Meth Acrylate	39.5
5	Benzoyl peroxide	0.5	Benzoyl peroxide	0.5	Benzoyl peroxide	0.5	Benzoyl peroxide	0.5	Benzoyl peroxide	0.45
6	Total	100	Total	100	Total	100	Total	100	Total	100



Reaction Scheme- 1

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Results and Discussion

FTIR

Fourier Transform Infrared Spectroscopy

FTIR analysis was carried out by using an ATR-FTIR spectroscope (Agilent Cary 630, Agilent, USA) of 650-4000 cm-1 toClassify functional groups and characteristic peaks.

The characteristics peaks at 751, 842, 986, 1141, 1440, 1724, 2951 and 3625 cm^{-1} shows RCH=CHR meta and mono substituted aromatic ring C-H stretching di-alkyl and aryl group. FTIR spectrums of CPS1-5 are given below numbering Fig 1 to 5 and comparison of IR is shown in Fig 6.

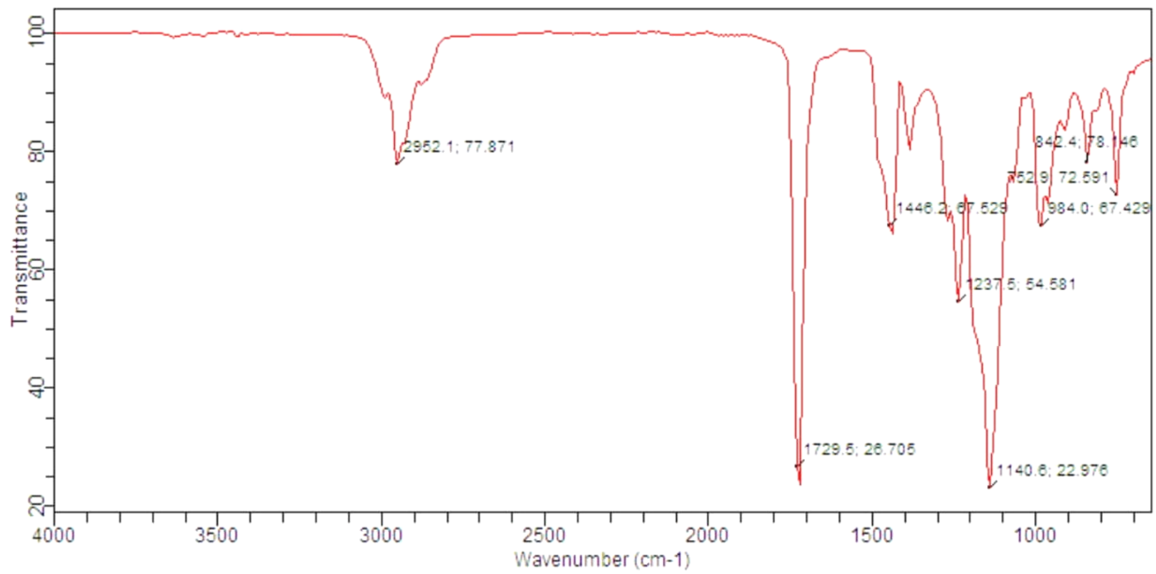

Fig. 1: FTIR SPECTRA OF CPS1.

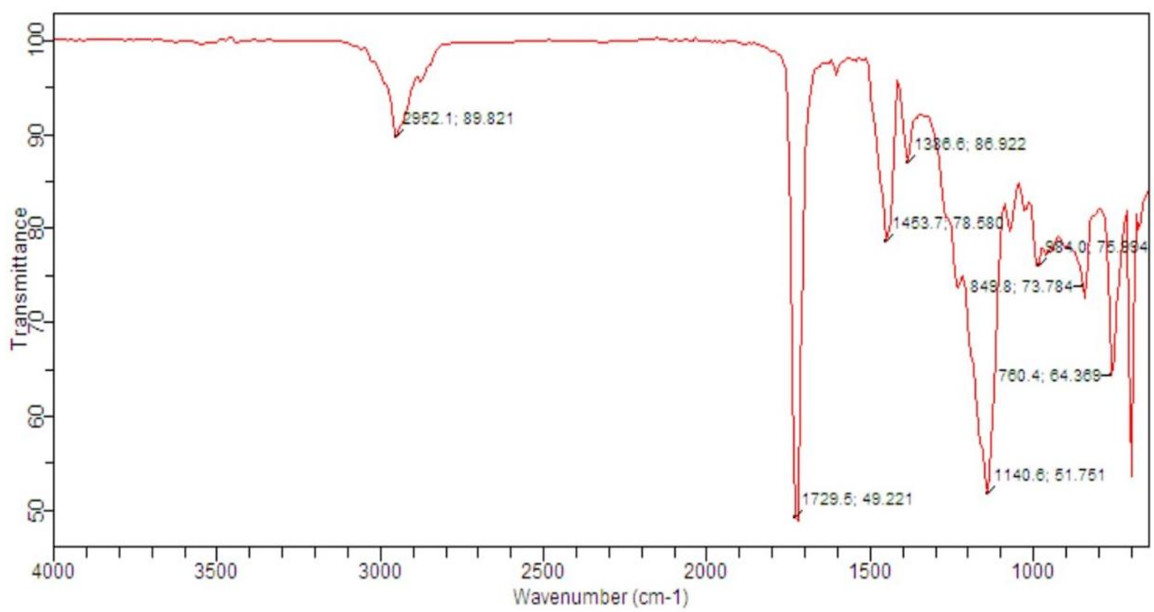

Fig. 2: FTIR SPECTRA OF CPS2.

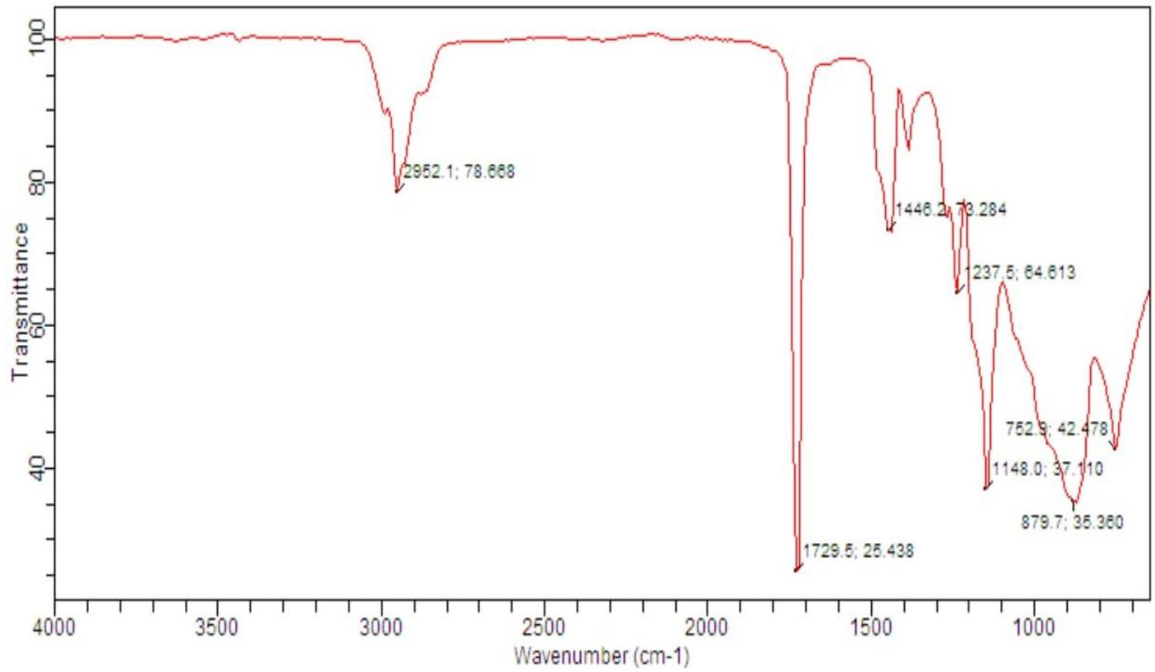

Fig. 3: FTIR SPECTRA OF CPS3.

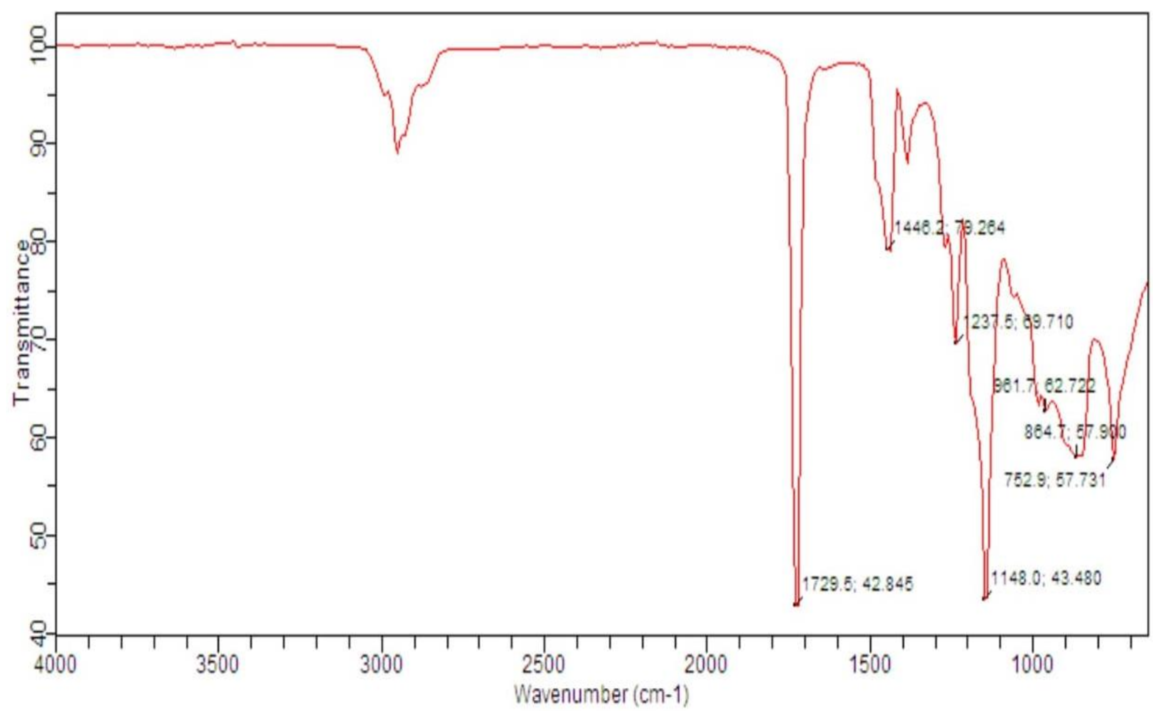

Fig. 4: FTIR SPECTRA OF CPS4.

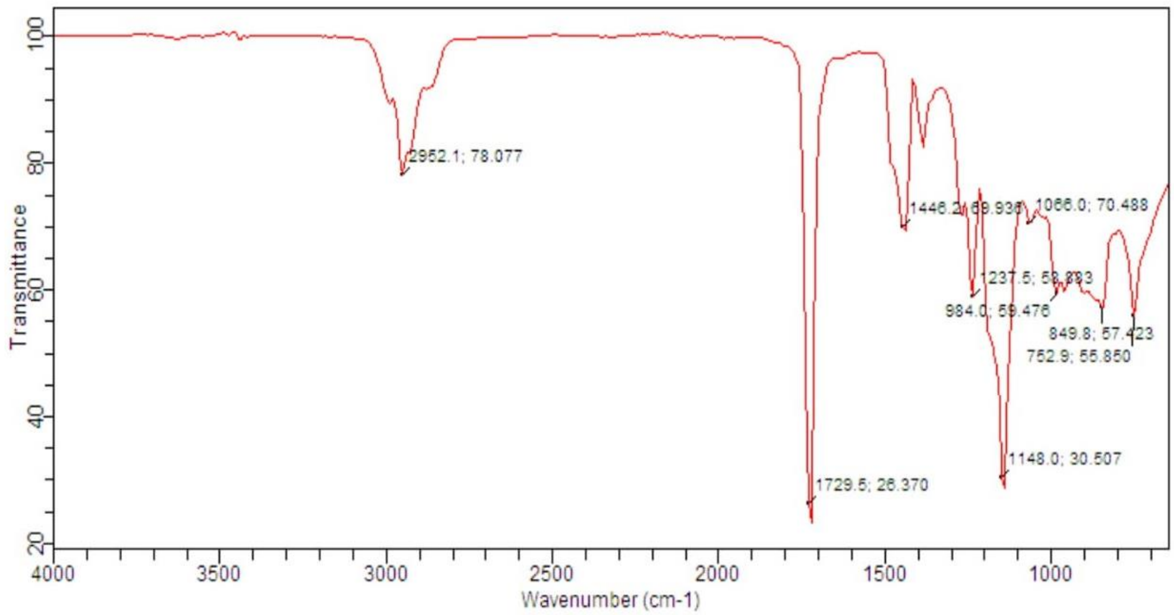

Fig. 5: FTIR SPECTRA OF CPS5.

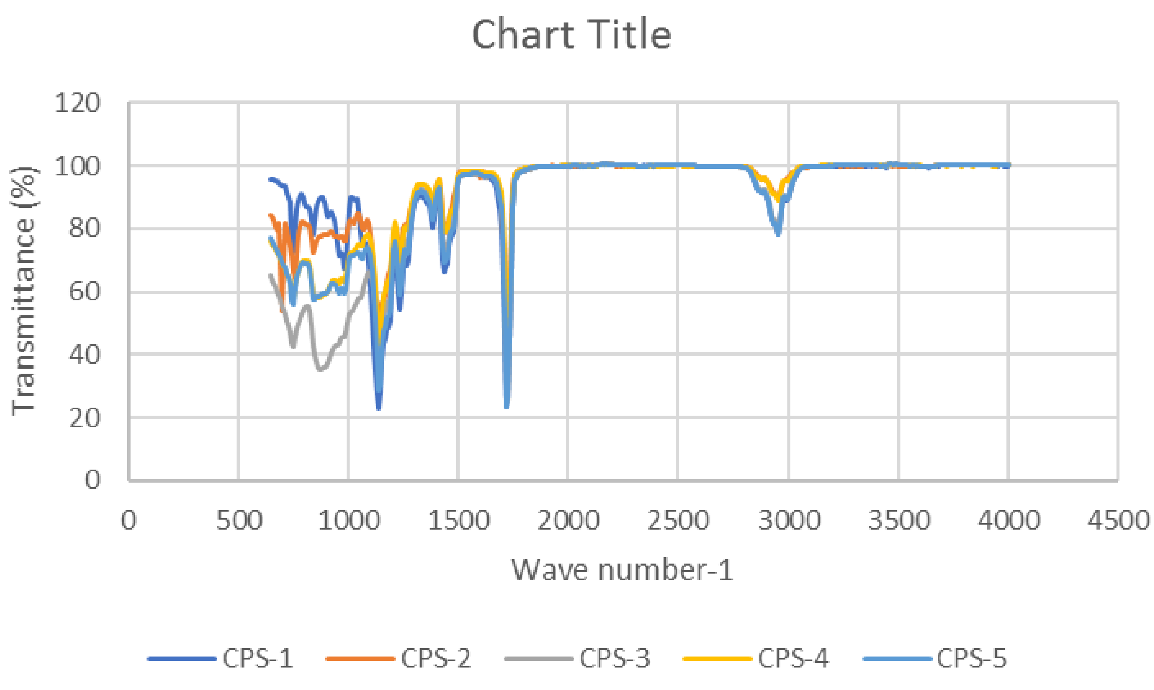

Fig. 1: Comparison of FTIR.

Antimicrobial activity

Antimicrobial activity of coated samples were tested against E.Coli by following Disk Diffusion Method followed by preparation of solid culture media, inoculation of coated sample and Bacterial colony onto the medium & their growth and observation of results and data collection. First of all 4g of nutrient broth and 7.5g of gum agar (purchased from Sigma Aldrich) along with 200ml of double distilled water was stirred for 5 minutes at 50^{o}C until all clumps of agar becomes invisible and added 300ml of distilled water and stirred for two minutes, autoclave at 121^{O}C for 15 minutes when temperature of the solution drops to 50 ^{O}C sterilized petri dishes were taken and about 20 ml the prepared agar media solution was poured and these media plates were incubated at 37 ^{O}C for 24 hours. Then bacterial culture and sample inoculation on to the prepared agar media was done along with coated samples then these petri dishes were again covered with lid, labeled and placed in incubator at 37 ^{O}C for 24 hrs. After that bacterial growth was observed and percentage inhibition was calculated in CFU/Mi log10 and percentage inhibition shown in Fig-7,8, Table2 and graphical representation in Fig-9.

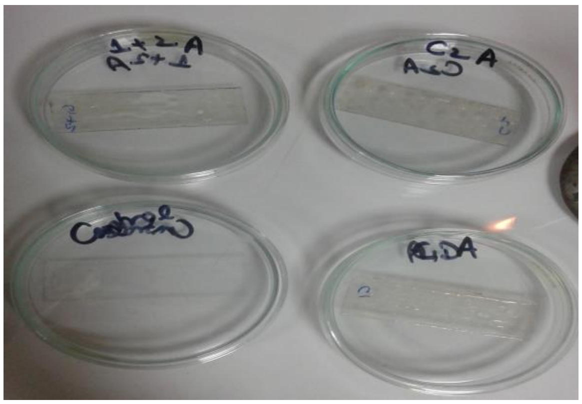

Fig. 7: Antimicrobial activity of coated sample.

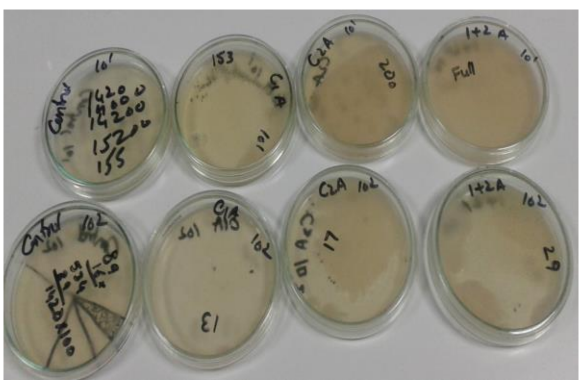

Fig. 8: Antimicrobial (%age inhibition).

Table-2: Antimicrobial activity.

Serial No.	Coating Material	% age inhibition
1.	control	100
2.	CPS-1	99.0
3.	CPS-2	98.8
4.	CPS-3	97.93
5.	CPS-4	98.7
6.	CPS-5	99.2

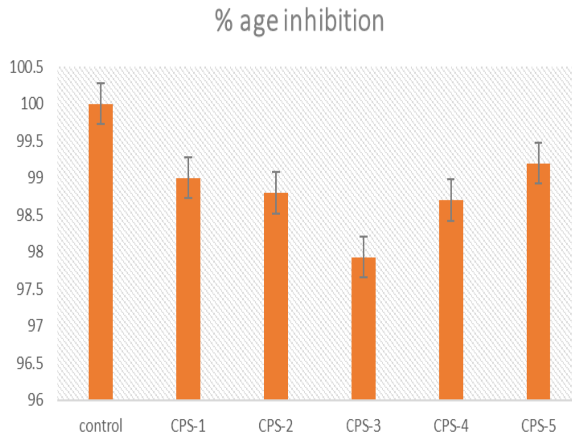

Fig. 9: Graphical Representation of Antimicrobial activity.

UV-Absorbance

Glass that is transparent to visible light absorbs nearly all UVB. This is the wavelength range that can cause sunburn, so it's true you can't get sunburn through glass. However, UVA is much closer to the visible spectrum than UVB. About 75 percent of UVA passes through ordinary glass. Glass filters out only one kind of radiation -- UVB rays. But UVA rays, which penetrate deeper, can still get through. That's why many adults have more freckles on their left side than their right -- it's from UV exposure on that side through the car window when driving. Graphs given below as Fig 10-14 and comparison in Fig15 showed that coating on glass is UV protected coating.

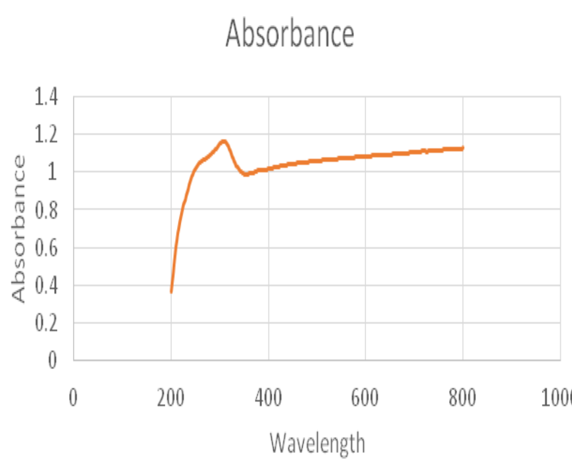

Fig. 10: UV-Absorbance of CPS-1.

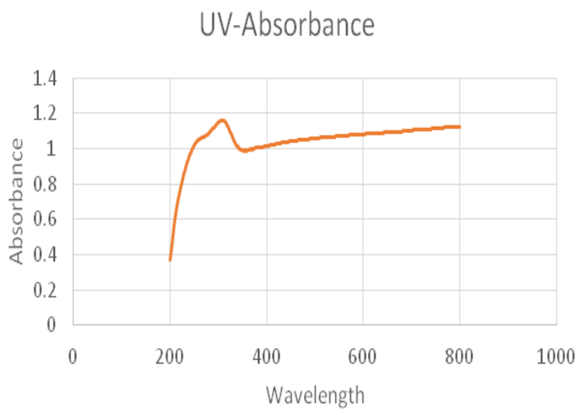

Fig. 11: UV-Absorbance of CPS-2.

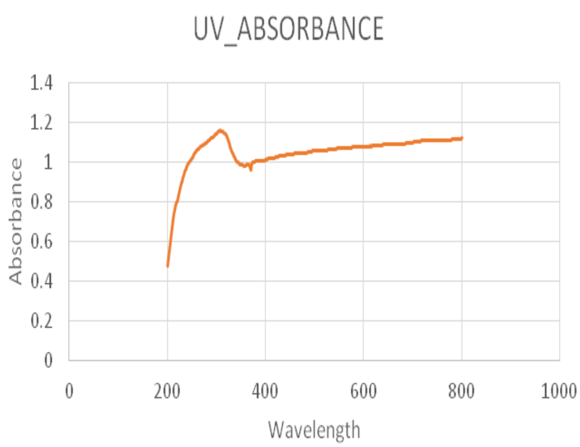

Fig. 12: UV-Absorbance of CPS-3.

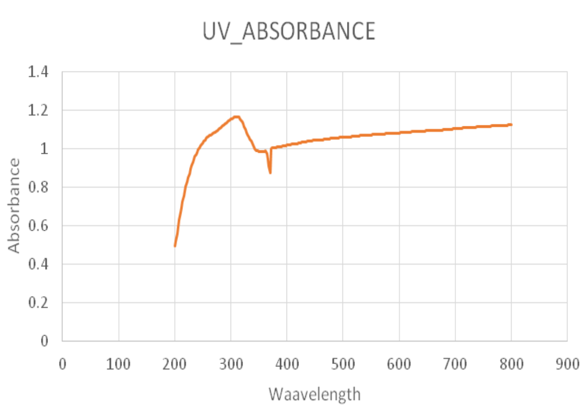

Fig. 13: UV-Absorbance of CPS-4.

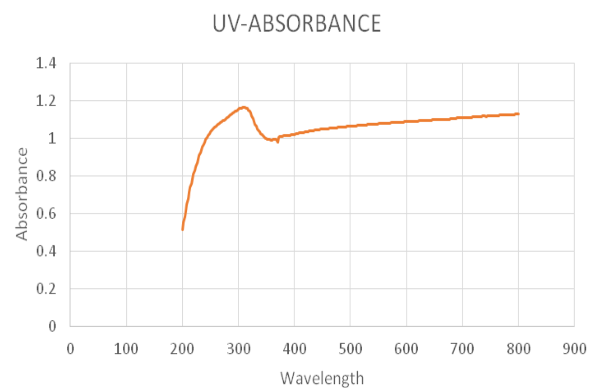

Fig. 14: UV-Absorbance of CPS-5.

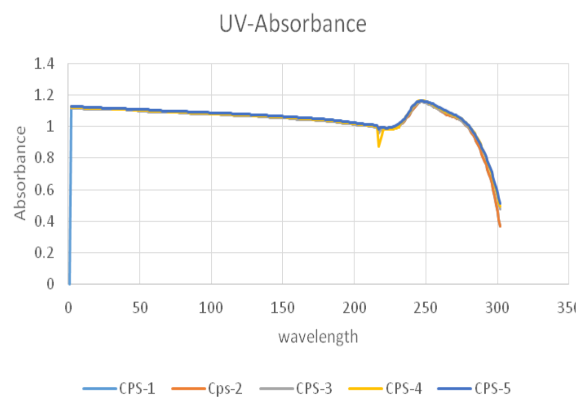

Fig. 15: Comparison of UV-Absorbance of CPS 1-5.

Contact Angle

Hydrophilic and hydrophobic behaviour was evaluated by measuring the contact angle of water droplet on the films under ambient conditions using the DSA30 Kruss Hamburg, Germany. The coating surface was placed and levelled on the test cell between the light source and microscope. Then 10μL water droplet was deposited onto the coating surface through a syringe. After the liquid drop reaches its equilibrium state, its digital image was recorded and the contour fitted by software. Detail is given in Table 3 and Fig 16.

Table-3: Contact Angle of Water on glass slides.

Sr.No.	Co-polymer	Contact angle
1.	**Control**	**45º**
2.	**CPS-1**	**93º**
3.	**CPS-2**	**79.7º**
4.	**CPS-3**	**84º**
5.	**CPS-4**	**87.3º**
6.	**CPS-5**	**88.5º**

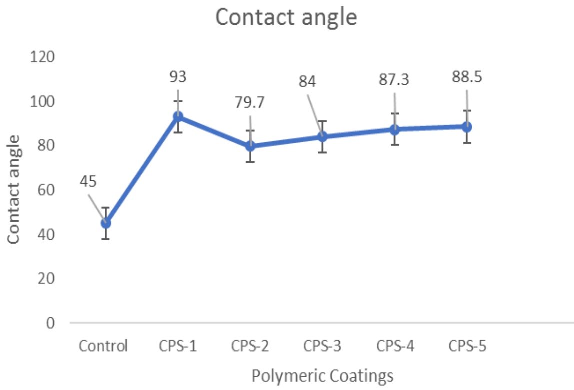

Fig. 16: Contact angle of CPS1-5.

Self-cleaning Property Test

Water droplets were dropped on slide which shoes hydrophobicity shown in Fig17. On coated and uncoated slides erected at an angle of 20^o mud, solution of methyl red, methyl orange and potassium dichromate was placed and observed that all stick on uncoated slides while coated slide due to its hydrophobic nature remained clean. Further due to the presence of Tio2 and Ag along with acrylate also undergoes photo-catalysis on coated surfaces resulting self cleaning

SEM Ananlysis

For surface morphology SEM analysis was performed and results are reported in Fig 19. As glass surface activated with propanol to increase surface roughness of glass then coated with developed material. SEM images sowing the presence of Tio2 and Ag on surface

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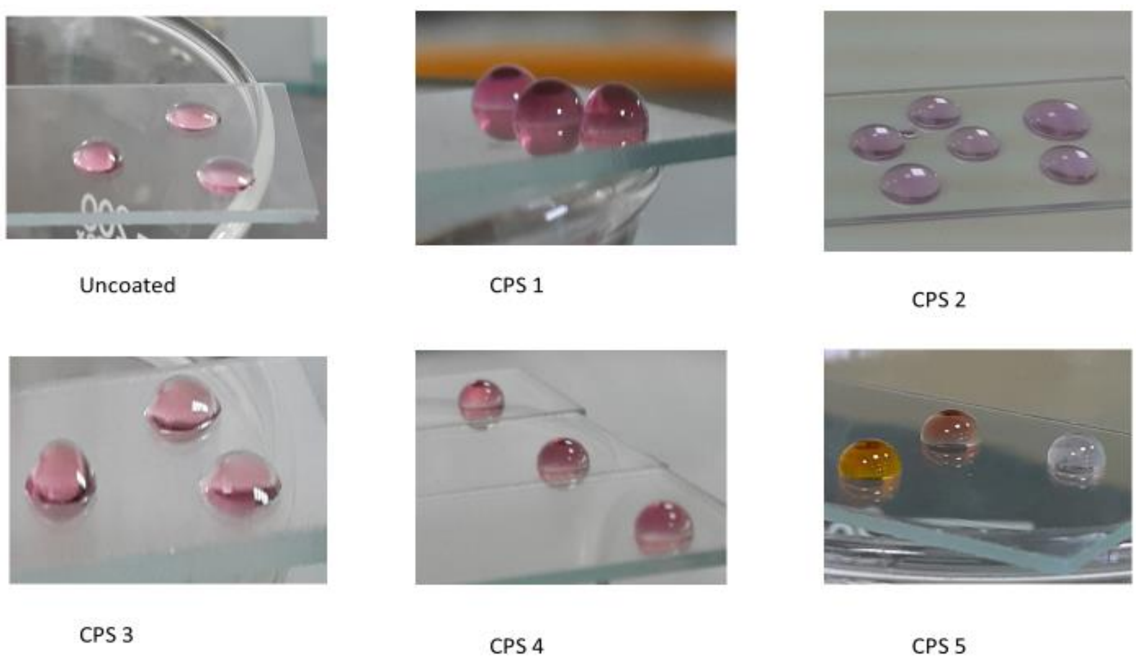

Fig. 17: Hydrophobicity on coated glass slides

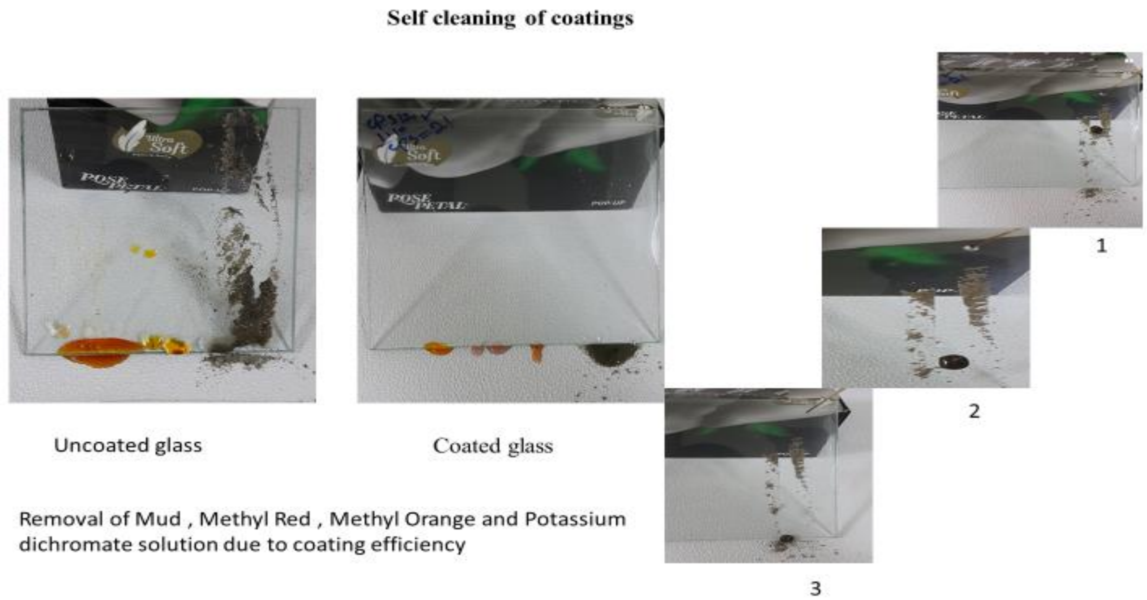

Fig. 18: Self cleaning ability of coated glass.

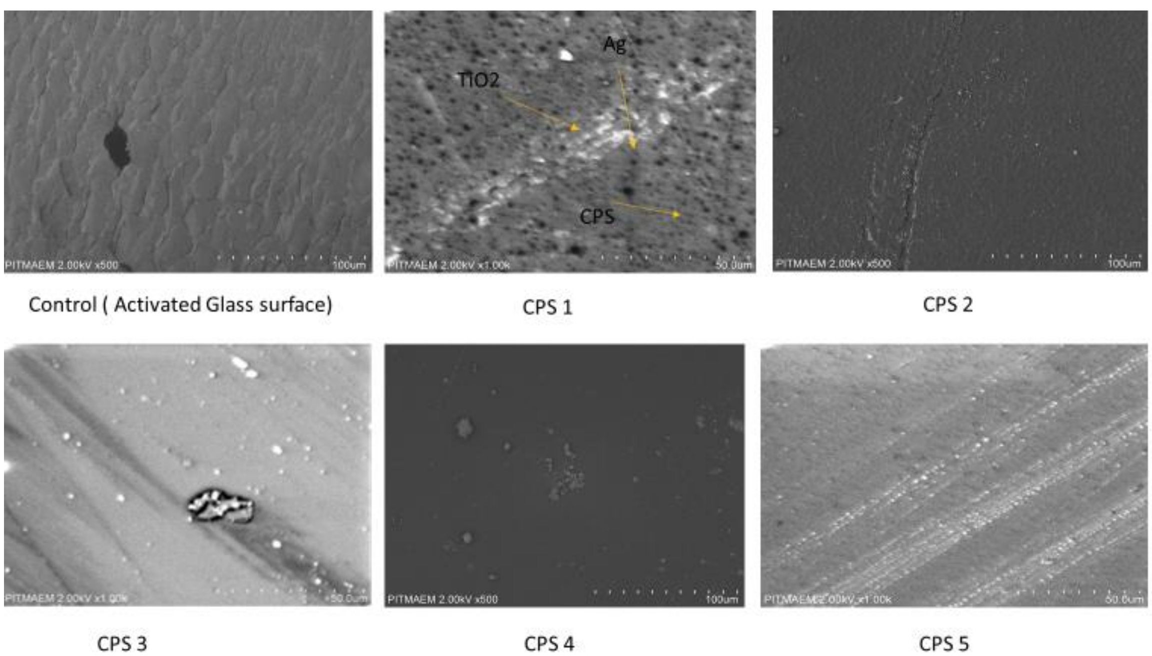

Fig. 19: SEM analysis.

The composite coating could be used to construct the meta composites with negative electromagnetic parameters to further elaborate the potential applications e.g.in the composites, of nickel and manganese showing tunneling nickel-networks. [30,31]. Recently silver nanowires developed and used in sensors for electronic devices. [32] There are many meta composites developed based on barium titanium and nickel showing potential applications in electromagnetic shielding and absorption [33].

Conclusion

The reported coating materials are good to protect against microbes and also provide UV protection and self cleaning activity. Results showed 99.2% inhibition of bacterial colony formation.

Water contact angle of bare activated glass slide is of 45º after surface activation while coated surface improved to 93º. The SEM images showed successful distribution of acrylates along with silver and TIO_2. Contact angle with different acrylate copolymers coating shown in table above. These are transparent coating which can be used easily on glass substrate by dip and spray coating methods. Further the coatings are antimicrobial, transparent and UV protected coatings.

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