Impact of Zinc Oxide on the UV Absorbance and Mechanical Properties of UV Cured Films

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Ultraviolet radiation [UVR]

- UVR is divided into UVC (200–290 nm), UVB (290–320 nm) and UVA (320–400 nm). UVA is further categorized as UVA I (340–400 nm) and UVA II (320–340 nm), also called long and short UVA respectively.
- UVR is generally credited with most of the biologically significant sequela of sun exposure like sunburn, skin cancer, and visible aging.

UV curable formulations

A UV curable formulation consists usually of multifunctional monomers and oligomers, with small amount of photoinitiator that generates reactive species on UV exposure.

Advantage of UV-cured systems

UV cured systems have both ecological and economical benefits over other kinds of systems and are widely used in various industrial sectors because of the following advantages:

- Great speed of cure
- Solvent free formulations
- High quality end products, and
- Room temperature operations
- Low energy consumption

Applications of UV-cured systems

This technology finds a large number of applications mainly in:

- Coating industry
- Printing inks
- Fast drying varnishes
- UV curable adhesives and as photoresist for imaging applications

Zinc oxide

- Zinc compounds can provide a variety of properties in the plastic field.
- Zinc oxide is outstanding among white pigments for its property for absorbing UV radiations.
- It offers broad spectrum coverage against UVA and UVB radiations

Objective of work

- The objective of the present work was to enhance the UV absorbance and to improve the mechanical properties of UV cured films that can be used as adhesives for lamination of the articles and also as protective coatings.
- Different UV curable formulations were developed by incorporating zinc oxide and then casted into thin films.
- These films were characterized for UV absorbance and mechanical properties and then compared with films cured in the absence of zinc oxide.

Development of formulations

- In these formulations the amount of divinyl ester resin was kept constant (56%) and the relative concentrations of monomers AA, MMA and EHA were changed.
- Two set of formulations were prepared one with zinc oxide and another without zinc oxide.
- Benzophenone was used as the catalyst [6% by weight] in each formulation. All the formulations were prepared in black colored containers and used for casting films.

Casting of films

- The first step involved in casting of the film is the mold preparation. The outer shell of the mold, i.e. the base and the upper cover, are made of one inch thick acrylic sheets. PET sheets were used to cover the surface of the acrylic. The use of PET sheet prevents the resin from sticking on to its surface while curing, so the film can be easily removed from the mold. The dimensions of the mold were 150×150 mm, including the double sided adhering tape, 10 mm in width and 2 mm in thickness.

- The second step involves pouring the liquid formulation into the cavity and then allowing to stand in the designed frame so that air bubbles are removed if present. Now at this stage pressure is applied by clamping the mold with the help of screws present in the designed frame. After ensuring that no defect is present in the filled mold the whole assembly is put into UV chamber. The cured film is then removed from the mold.

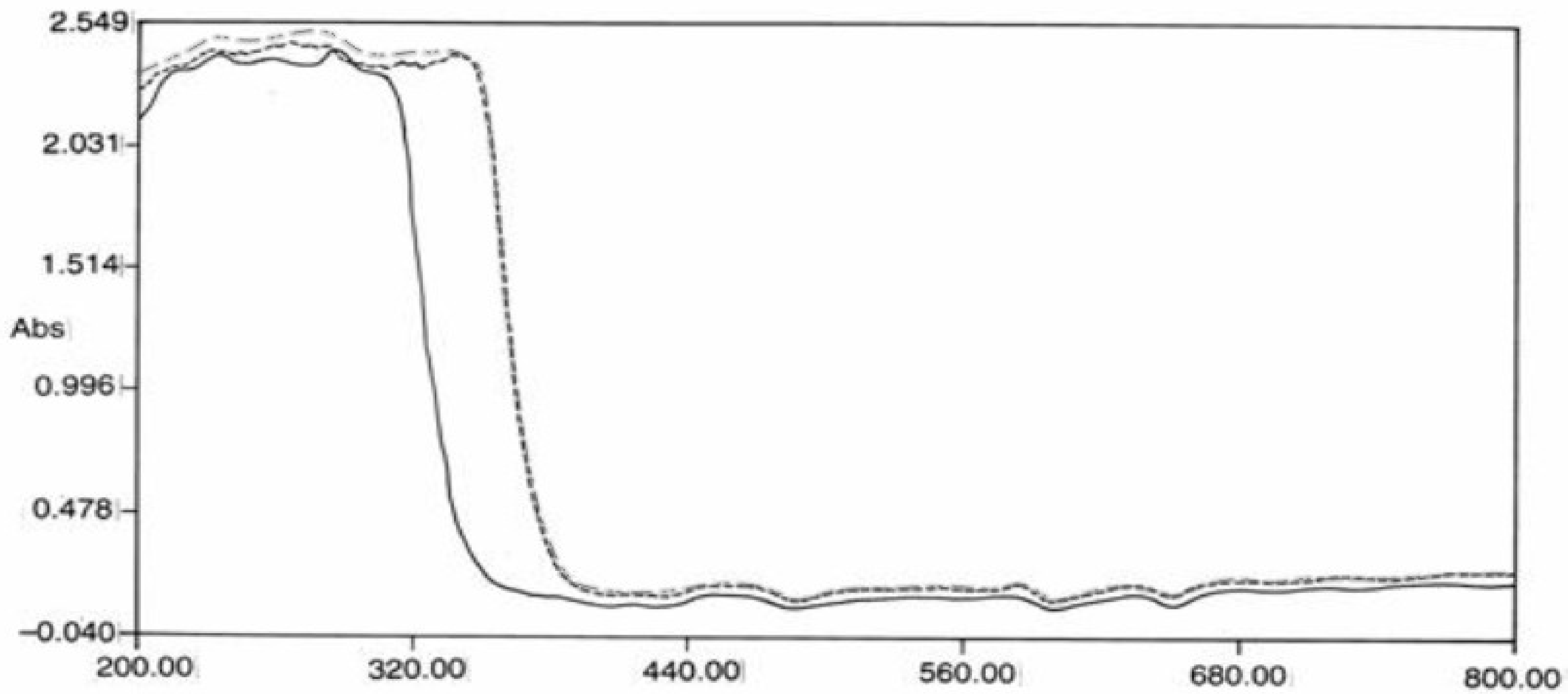
Table 1. Composition of the formulations developed by using divinylester resin (VER); methylmethacrylate (MMA); 2-ethyl hexyl acrylate (EHA); acrylic acid (AA) and benzophenone

S. no.	Desig-nation	VER (gm)	AA (gm)	MMA (gm)	EHA (gm)	Benzophenone (wt.%)
1	S_1	100	24	36	12	6
2	S_2	100	12	36	24	6
3	S_3	100	36	24	12	6
4	S_4	100	36	12	24	6

Table 2. Composition of the formulations developed by using divinylester resin (VER); methylmethacrylate (MMA); 2-ethyl hexyl acrylate (EHA); acrylic acid (AA); ZnO and benzophenone

S. no.	Designation	VER (gm)	AA (gm)	MMA (gm)	EHA (gm)	Benzophenone (wt.%)	ZnO (wt.%)
1	SZ_1	100	24	36	12	6	0.1
2	SZ_2	100	12	36	24	6	0.1
3	SZ_3	100	36	24	12	6	0.1
4	SZ_4	100	36	12	24	6	0.1

Fig. 1. UV-visible absorption spectrum of ordinary glass (─), a 2 mm thick interlayer glass laminate (--) with reference to air, showing enhancement of UV absorption in the laminated assembly with UV cured film (SZ_2) and 2-mm thick interlayer glass laminate with ZnO



UV absorbance

- 98.7% of the UV radiation that reaches the earth's surface is UV-A.
- In the past UV-A radiation was considered less harmful, but now it is known that it can contribute to skin cancer through indirect DNA damage.
- UV-A does not damage DNA directly like UV-B and UV-C, but it can generate highly reactive chemical intermediates, such as hydroxyl and oxygen radicals, which in turn can damage DNA.
- The UV cured films of the present work absorbs in the region 200–385 nm hence blocking 85% of the UV radiation above 300 nm.

Mechanical properties of the UV cured films

- The hardness of UV cured films was determined with the help of Durometer-D (ASTM D 2240 Shore-D).
- The tensile properties of the casted films were determined as per the ASTM D 638 with the help of ZWICK UNIVERSAL TENSILE TESTING MACHINE (CAP.5 KN) (M1435). The value of tensile strength and % elongation at break was calculated by following equations:
- Tensile Strength = Value of load / Thickness × Width
- % Elongation at break = (Final length – Initial length / Initial length) × 100

Table 3. Hardness (Shore D); percentage elongation; tensile modulus and tensile strength of 2-mm thick interlayers prepared by UV curing

S. no.	UV cured films	Hardness (shore D)	Percentage elongation	Tensile strength (kg/cm^2)
1	S_1	80	4.37	156.58
2	S_2	78	6.50	199.07
3	S_3	81	4.12	193.72
4	S_4	79	4.95	196.54
5	SZ_1	78	4.50	204.65
6	SZ_2	74	6.65	284.16
7	SZ_3	77	4.72	246.67
8	SZ_4	75	5.15	271.83

Fig. 2. Hardness vs. EHA concentration in UV cured films

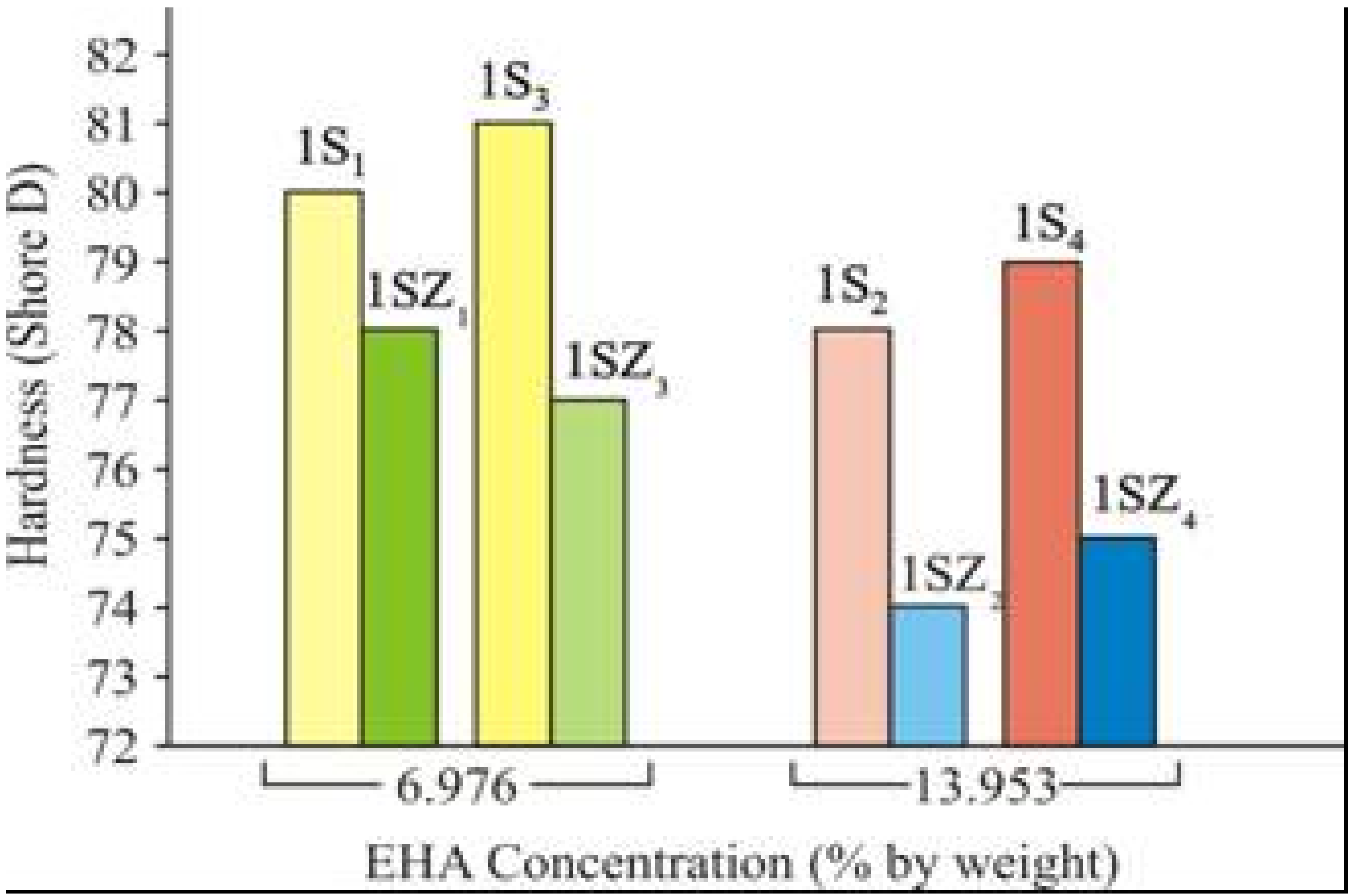


Fig. 3. Tensile strength vs. UV cured films

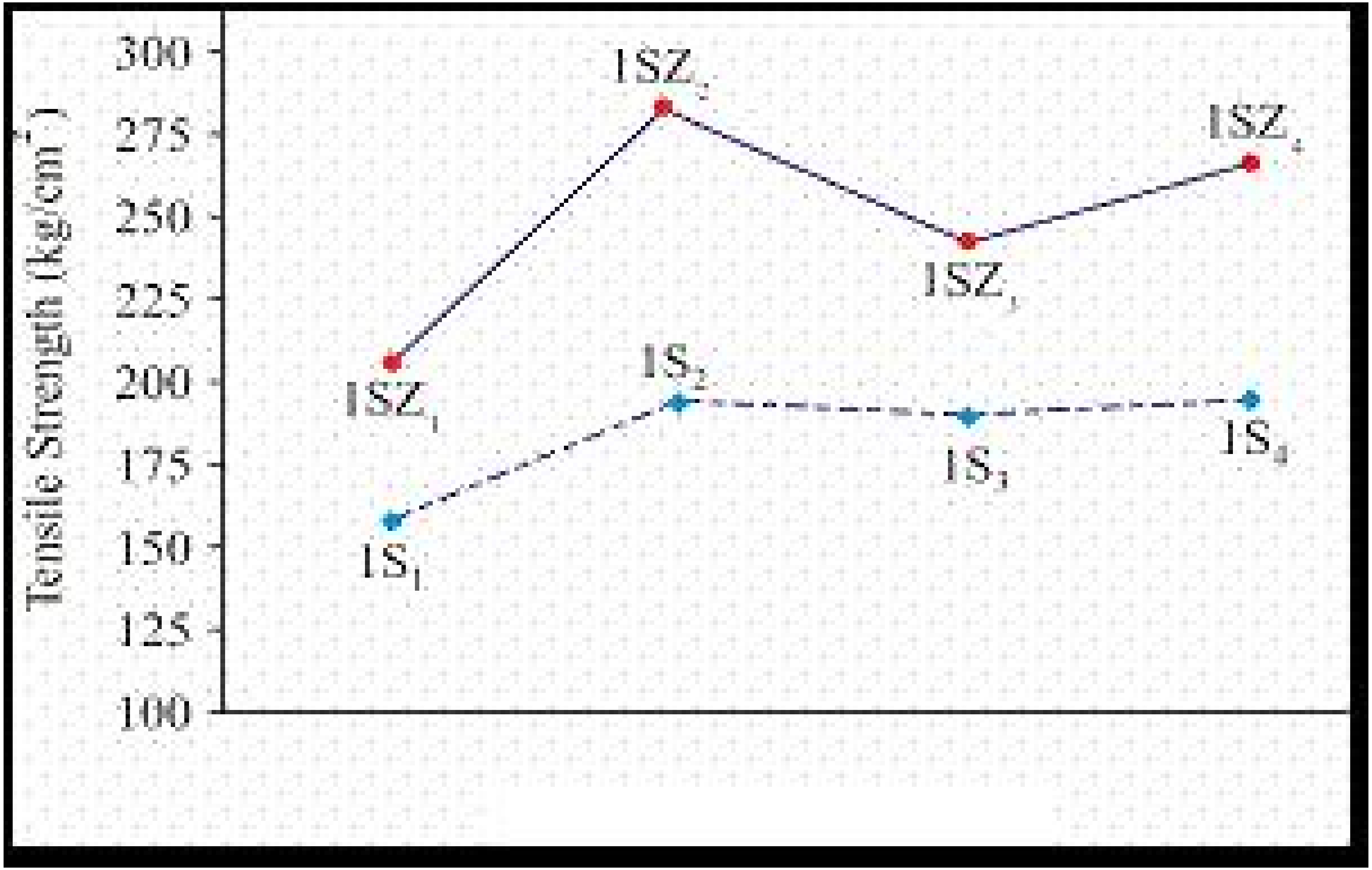


Fig. 4. Percentage elongation EHA concentration in UV cured films

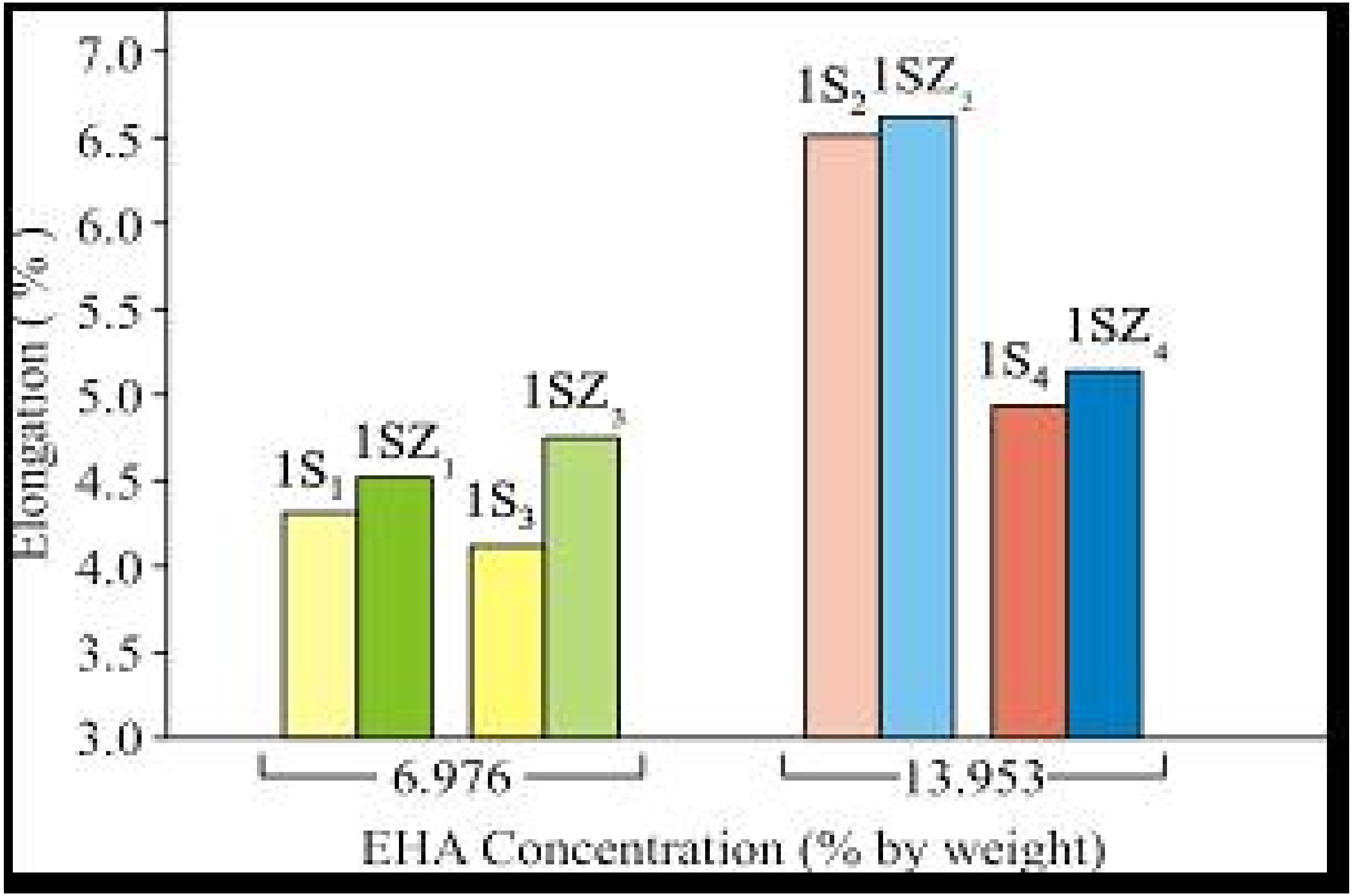
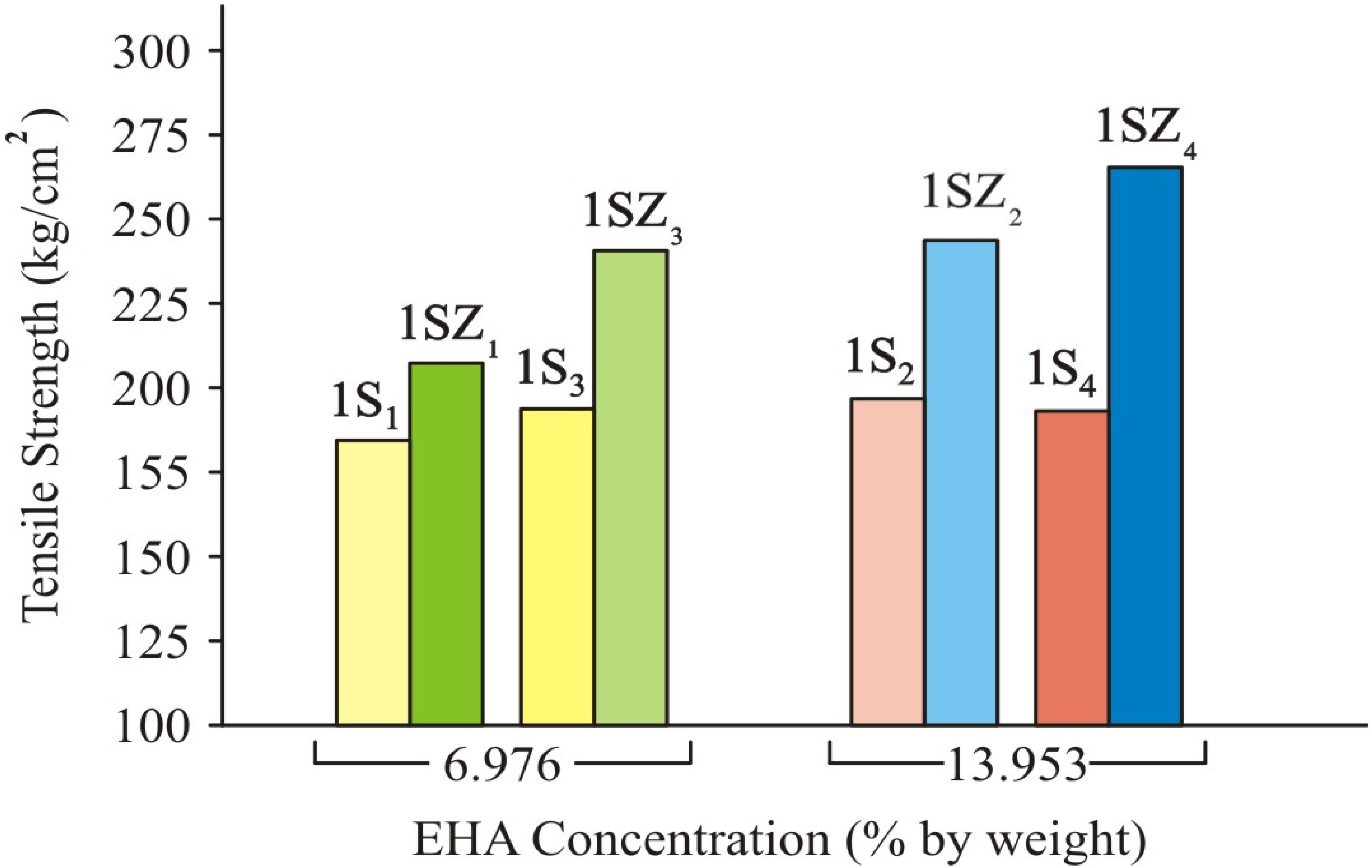


Fig. 5. Tensile strength vs. EHA concentration in UV cured films

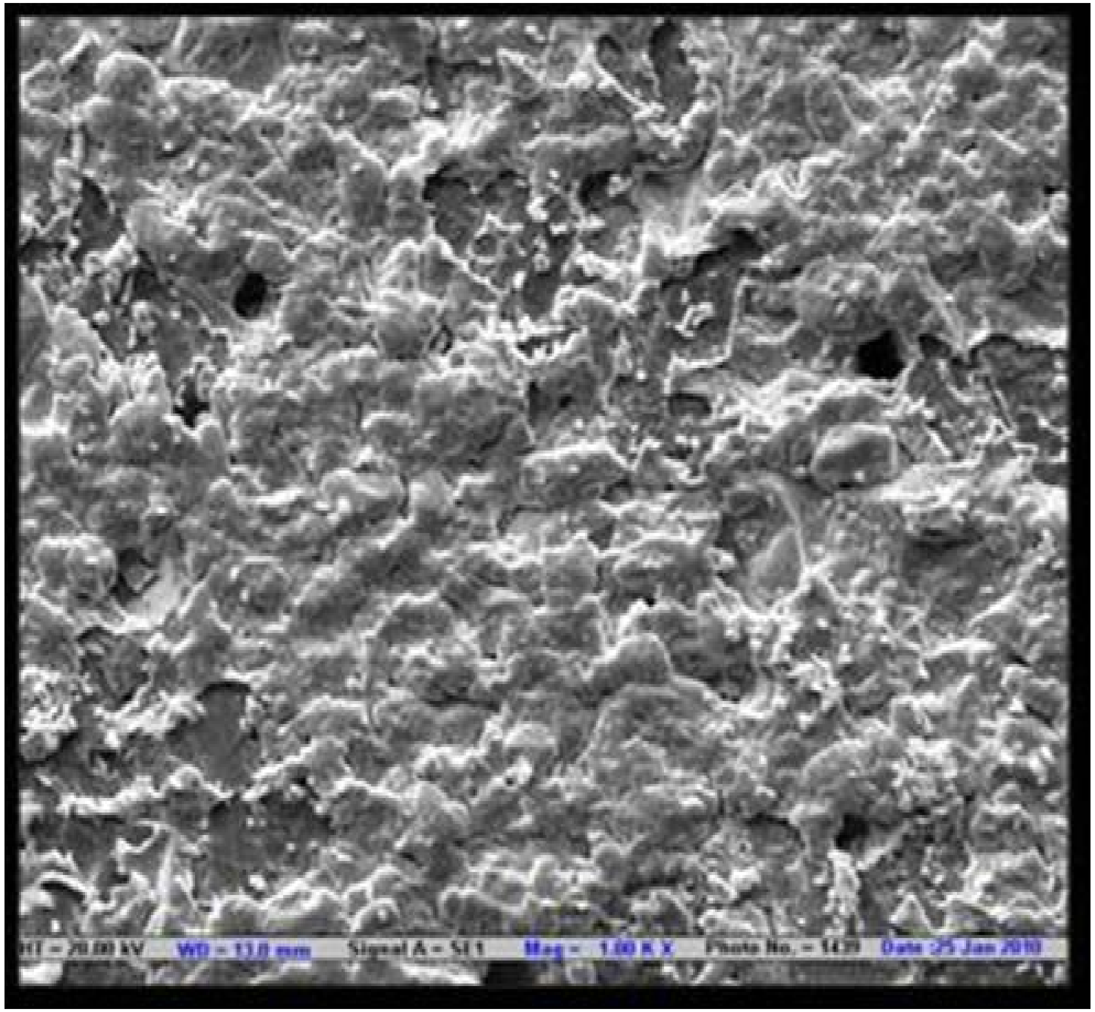


SEM studies of the interlayers

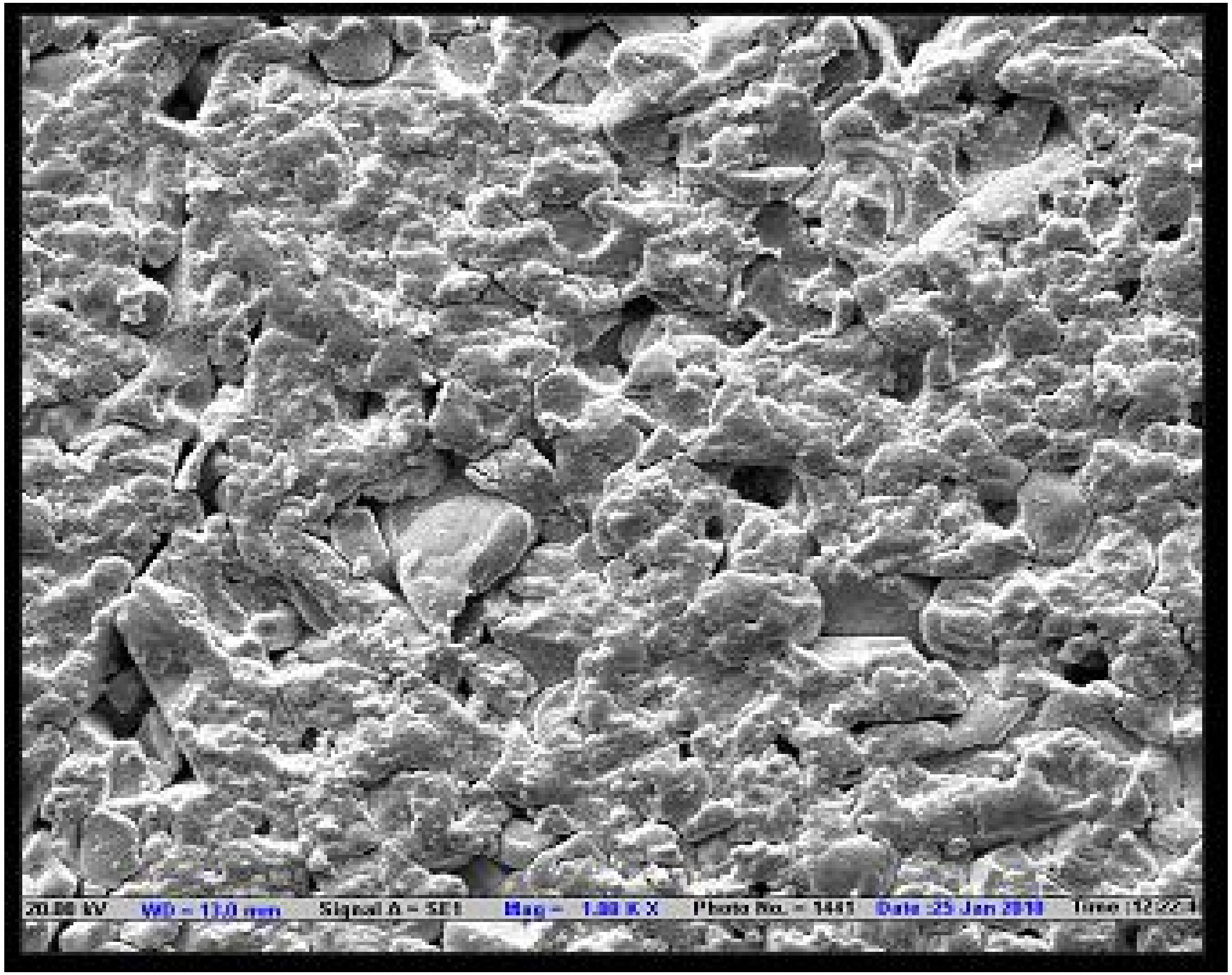
- SEM studies were done on JEOL JSM- 840 scanning electron microscope.
- The small pieces of casted films were plated with 22 carat gold and photographed at desired magnification.
- The surfaces of the cured interlayer were compared with the help of scanning electron micrographs.

SEM micrograph of IS_2 film

- It shows voids with roughness on the surface.
- However, the polymerization does not show separation of phases and presents a continuous surface. Similar kind of behavior was observed for interlayer IS_4

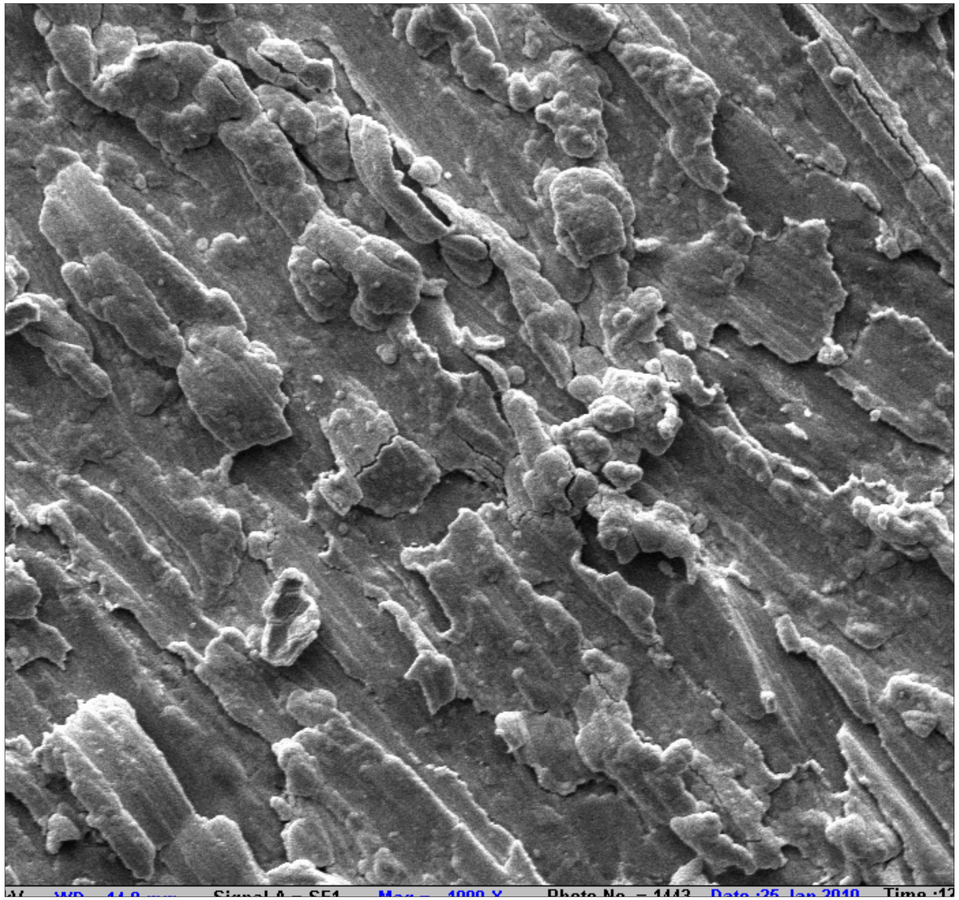


SEM micrograph of IS_4 film



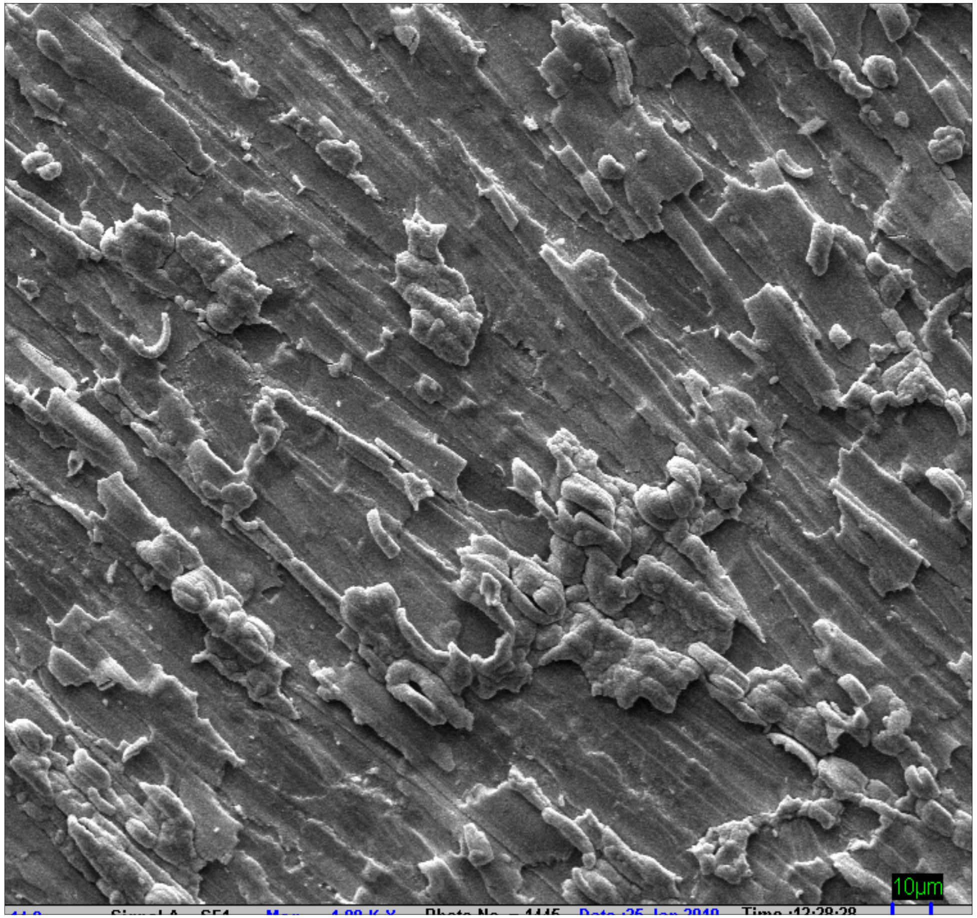
SEM micrograph of ISZ_2 film

- polymerization under the influence of zinc oxide.



SEM micrograph of ISZ_4 film

- A continuous, voidless surface was observed.
- However the surface is not uniform and smooth but still does not show any phase separation and offer good adhesion with excellent mechanical properties.



CONCLUSIONS

- Novel UV curable formulations have been developed to obtain UV cured films by a process that is faster, cheaper and easier to work out than the usual thermal cure carried out under high pressure.
- The photoinitiated polymerization of acrylate monomers has been utilized to produce cross linked polymers suitable for adhesive applications.

- The presence of zinc oxide in these formulations was found to enhance the UV absorbance and a remarkable improvement was obtained in the mechanical properties of UV cured films.
- The developed formulations could be utilized for laminating different substrates and also as protective coatings in different applications to minimize the harmful effects of UV-A radiation present in direct sunlight.

THANK YOU