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# Synthesis, and Characterization of Ethyl Methacrylate based $ZrO_2$ Nanocomposites

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## 1. INTRODUCTION

N- Vinyl carbazole is an organic compound that is utilized as a monomer for the production of Poly(N-Vinyl carbazole). It is used is photoreceptors, in photocopies. NVC is a saturated hydrocarbon with a helical structure due to aromatic carbazole. Pendant groups is a thermoplastic of conjugated polymer with high thermal and chemical stability. It has high refractive index [1]. These characteristics are useful to electroluminescent devices and photorefractive material [2-4]. Poly(NVC) is also used as hole transparent layer in organic light emitting diodes [5-9]. The presence of a heterocyclic ring system in N-Vinyl carbazole imparts it with effective corrosion inhibition properties. N-Vinyl carbazole, have good thermal stability, high dielectric constant and exhibit photo conductivity. It seems reasonable, therefore to modify the thermal properties of methacrylate by preparing copolymers with N-Vinyl carbazole. The growing interests in these organic polymers are due to their characteristic architectural features, which provide the end products with enhanced properties as compared to materials and wider applications.

The advantage of methacrylate based polymers is its high thermal, chemical and mechanical stability, which makes them best candidate for applications that require adhesion to various substracts, abrasion resistance, flexibility, toughness and excellent resistance to chemicals, solvents, and water. The degradation temperature of such polymers could have high temperature as 500 $^0$C. In addition, it has high molecular weight and mechanical stability of methacrylate based polymers, low thickness films metallic surface.

$ZrO_2$ (zirconia) is a valuable material with various applications, including as a semiconductor, dielectric material, and in energy conversion systems. It has good natural color, high strength, transformation toughness, high ion exchange capacity and resistance to corrosion, chemicals, and microbes [10 - 12]. $ZrO_2$ nanoparticles are useful in transistors [13], optical applications [14], fuel cells and as sensors [15, 16]. It has three crystal phases, cubic, tetragonal, and monoclinic, at different temperatures [17, 18]. Monoclinic is stable up to 1100°C, tetragonal exists between 1100°C and 2370°C, and cubic is present at temperatures above 2370°C.

Several techniques are available for producing zirconia nanoparticles, such as sol/gel method [19], vapor phase method [20], pyrolysis [21], spray pyrolysis [22], hydrolysis [23], hydrothermal [24], and microwave plasma [25]. These methods have limitations such as complicated procedures, high reaction temperature, long reaction time, toxic reagents, by-products use, and high production cost, making large-scale $ZrO_2$ nanoparticle production difficult. Organic coatings were employed for the protection of materials from the exposure of UV radiation. The exposure of UV-radiation to organic coating surface may accelerate/cause significant degradation, which is responsible for the discoloration of dyes and pigments, weathering, yellowing of plastics, loss of gloss and mechanical properties, etc. Therefore, designing and development of UV-shielding materials attracts significant research interests in coating technology. A suitable anticorrosive and UV absorbing moiety has to be fabricated that can play a synergistic action, i.e. designed hybrid material should behave as UV-shielding coatings. Thus, there is a demand to design a functionally active polymer hybridized with photoactive metal oxide nano fillers for UV shielding applications. The engineering of polymeric hybrid, can be achieved using functionally active polymer with optically induced nano-filler.

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In the present work, an attempt has been taken to report the UV blocking efficiency of highly charged polymer namely Poly(NVC-co-EMA) and its nano composites with $ZrO_2$, The above choose nano particles are photovoltaic materials which is responsible for UV shielding applications.
Zirconium nanoparticles, and methacrylate were purchased from Sigma Aldrich, India, (EMA) Ethyl methacrylyte (sigma-Aldrich) was distilled under reduced pressure to remove inhibitors and stored in refrigerator. Benzoyl peroxide (BPO) was re-crystallized from chloroform-Hexane (1:1), AIBN (Azobisisobutyronitrile sigma Aldrich, India) was crystallized from ethanol at 50 $^0$C [26]. chlorobenzene, hexane acquired from Merck was dried by sodium metal before use. All the other chemicals were procured from Merck and purified by standard methods.

**Synthesis of Copolymer of Poly (NVC-co-EMA):**
Predetermined quantities of the monomers Ethyl methacrylate and N-vinylcarbazole, along with 2,2' azobisisobutyronitrile (AIBN) were dissolved in 25 ml of Chlorobenzene placed in a standard reaction tube to be obtained a homogeneous solution. Dry nitrogen gas without oxygen was used to flush the mixture. The inlet and outlet of the reaction tube were closed by means of rubber tubing and pinch cork. The reaction vessel is then immersed in a thermostatic water bath maintained at 65 $^0$C. The copolymerisation reaction was allowed to proceed for an appropriate duration, the copolymerisation reaction was stopped. The solution is poured into excess hexane to precipitate the copolymer. The copolymers were purified by repetitive precipitation using hexane from a chloroform solution. It was then dried in vacuum over at 40 $^0$C for 24 hours.

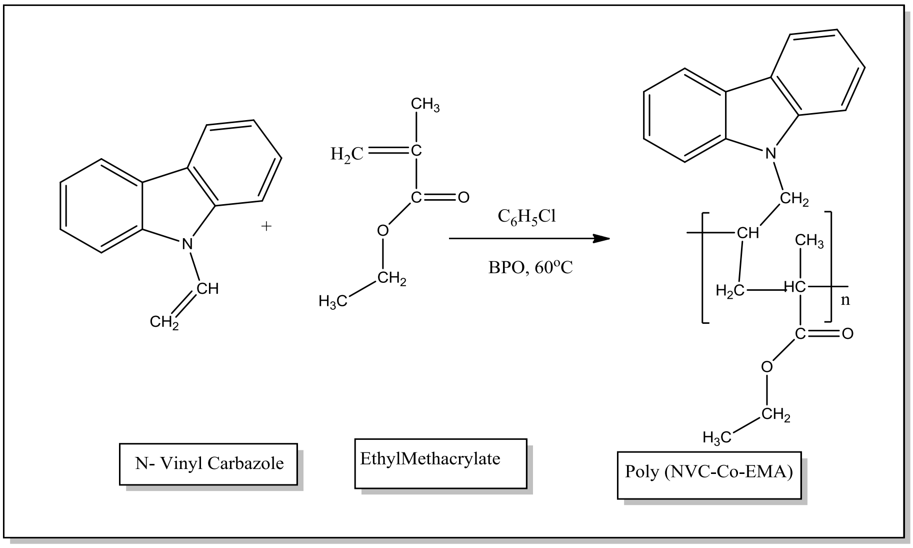



Fig. 1. Scheme of the Preparation of Poly (NVC-co-EMA)/$ZrO_2$

**Preparation of Poly (NVC-co-EMA)/$ZrO_2$**
The NVC and Ethyl methacrylate/$ZrO_2$ (2, wt% $ZrO_2$) was prepared by solution polymerization. Poly (NVC-coEMA)/$ZrO_2$ was prepared by the addition of 10 m mol of (NVC-methyl methyl methacrylate and 2, wt% of $ZrO_2$ in Chlorobenzene solvent. After sonication for 30 min, polymerization is done at 60 $^0$C using AIBN as radical initiator under $N_2$ atmosphere for 2hr. After cooling, white coloured amorphous powder was obtained by the addition of hexane, it was further reprecipitated from chloroform to get the pure product (Scheme 1). Same experimental procedure was followed to synthesize Pure Poly (Vinyl carbazole) polymer without $ZrO_2$ Nps.

**Characterization techniques:**
1. The FT-IR Spectrum for the Poly (NVC-co-EMA)/$ZrO_2$ was recorded in order to confirm the structure of the polymer.

2. The Poly (NVC-co-EMA and its $ZrO_2$ nanocomposites were characterized by XRD (Bruker-D8 Advanced X-ray diffractometer with Cu-Ka (1.5418 A)
3. The UV visible transmission spectra were recorded on JASCOeV-670 spectrophotometer in the wavelength range 300-800 nm to investigate the optical properties of the nanocomposites.

## 2. RESULTS AND DISCUSSION

### FT IR Spectroscopy

The FTIR spectra (Fig. 3) of $ZrO_2$NPs show a broad band with low intensity at 3049.48 $cm^{-1}$ relate to the vibration mode of –OH, indicating the presence of moisture adsorbed on the $ZrO_2$NPs. The band at 530.42 $cm^{-1}$ corresponds to O-Zr-O bond. The FTIR spectra of Poly (NVC-co-EMA)/$ZrO_2$ display a band at 748.38 $cm^{-1}$ was assigned to –C=O stretching vibration of ester group. The C–N stretching is sensed at 1388 $cm^{-1}$. The FTIR spectra of Poly (PVC-co-EMA)/$ZrO_2$ (Fig. 3) show the same Poly (PVC-co-EMA)/$ZrO_2$ characteristic peaks with an additional band at 452.23 $cm^{-1}$, corresponds to O-Zr-O. However, there is evidence for the decrease in peak intensity due to the addition of $ZrO_2$ in the Poly (PVC-co-EMA)/$ZrO_2$. This observation clearly explains about the good compatibility, "arising" between the counterparts $ZrO_2$ and Poly (PVC-co-EMA)

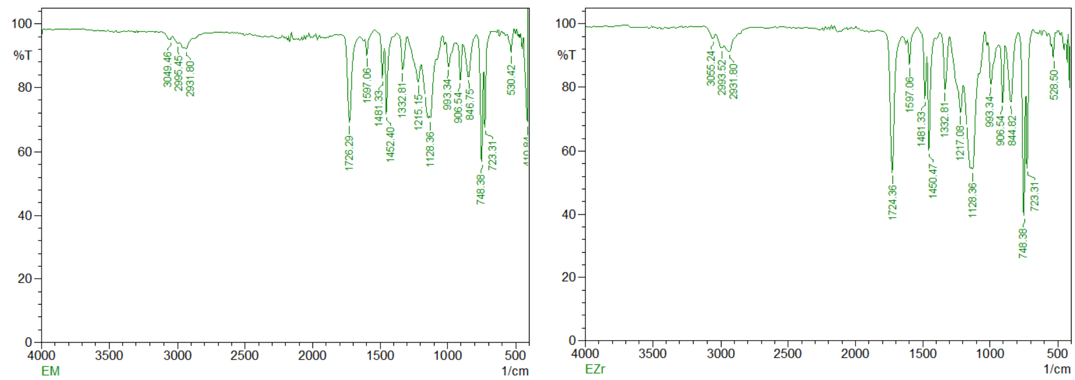
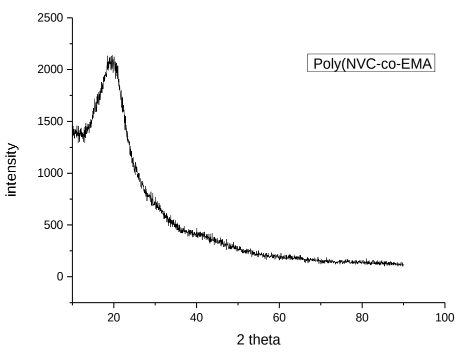



Fig. 2 FT IR spectra of Poly (NVC-co-EMA), Fig. 3 FT IR spectra of Poly (NVC-co-EMA)/$ZrO_2$

### XRD Studies

The crystallinity of pristine $ZrO_2$ NPs was analyzed by X-ray diffractograms (Fig. 4). The sharp diffraction peaks at 2θ =20 (2230), 23(1750), 30(870), 40(520) demonstrate the crystallinity and hexagonal wurtzite structure of $ZrO_2$ NPs which is in accordance with the standard JCPDS file no 36-1451. To know the effect of surface treatment on the crystalline size of nanoparticles, the XRD pattern of $ZrO_2$ was taken. The diffraction peaks of these two profiles are consistent with typical wurtzite structure of $ZrO_2$. The XRD patterns of the pure Poly (NVC-co-EMA) and Poly (NVC-co-EMA)/$ZrO_2$ were recorded to study the effect of $ZrO_2$ incorporation in the Poly(NVC-co-EMA). The XRD pattern Fig. 4 shows a broad non-crystalline peak at 10–15°, confirms the amorphous nature of Poly (NVC-co-EMA). The presence of all the characteristic diffraction peaks of $ZrO_2$ NPs in Fig. 4.2b, confirms the incorporation of it. The XRD pattern of Poly (PVC-co-EMA)/$ZrO_2$ shows the co-existence of broad amorphous peak (10–30°) of the Poly (NVC-co-EMA) and crystalline peaks (30–80°) of $ZrO_2$ NPs.



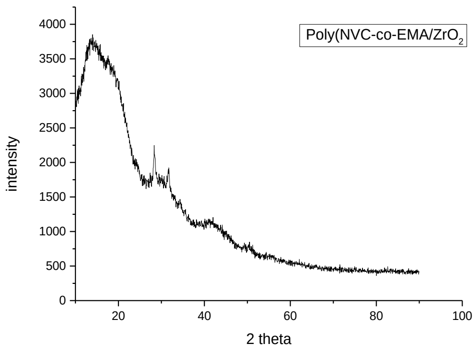
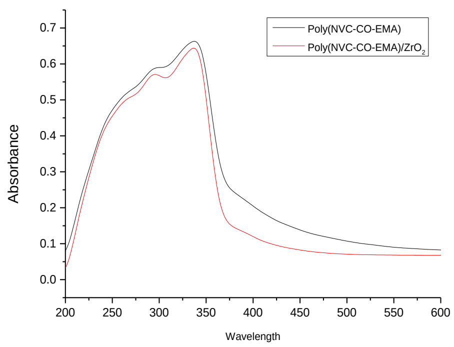




Fig: 3 XRD spectra of Poly(NVC-co-EMA), Fig: 4. XRD spectra of Poly (NVC-co-EMA)/$ZrO_2$

**UV Spectroscopy**
**Absorbance**

To investigate the optical properties, the absorption spectra of the Poly (NVC-co-EMA) and Poly (NVC-co-EMA)/$ZrO_2$ (5wt %) of $ZrO_2$ loading were taken and shown in Fig. 5. The absorption spectrum of pure Poly (NVC-co-EMA) has shown one broad absorbance band at 325 nm, which is assigned to the p-p* electronic transitions of N-vinyl carbazole moiety. The absorbance spectra of the Poly (NVC-co-EMA)/$ZrO_2$ showed an additional absorbance band at 325 nm corresponding to $ZrO_2$ nanoparticle. Fig. 5 indicates that the absorbance of nanocomposite increases with the increase of $ZrO_2$ NPs content, which is comparable with $ZrO_2$ NPs doped in functional conducting polymers.



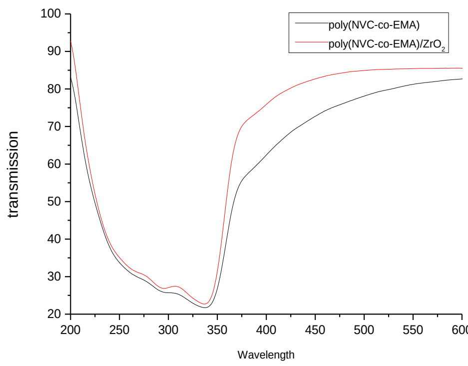




Fig: 5 UV absorption Spectra of Poly (NVC-co-EMA) & it's $ZrO_2$ nanocomposites
Fig: 6 UV transmission Spectra of Poly(NVC-co-EMA) & it's $ZrO_2$ nanocomposites

The increase in UV absorbance is due to the absorption of incident radiation by free electrons of $ZrO_2$ NPs and get excited to the Poly($ZrO_2$-co-EMA). It is well known that the N-Vinyl carbazole moiety possesses strong electron acceptor character, therefore the Poly(NVC-co-EMA)/$ZrO_2$ can improve the UV weather ability of the polymer film and the undercoats. As a result, it can be potentially applied to UV-shielding materials such as fibres and coatings.

**Transmission:**

The transmittance spectra of Poly(NVC-co-EMA) and its $ZrO_2$ nanocomposite films with 5wt%$ZrO_2$ filler contents transmittance at two different wavelengths, that is at 350 and 450 nm. The incorporation of 5wt% $ZrO_2$ decreases the transmittance of the resultant nanocomposite at UV region. Hence the increase in $ZrO_2$ NPs percentage in the nanocomposite, increases the UV absorption light at 350-400 nm. The 5wt% $ZrO_2$NPs loading in showed 20% of transmittance in UV region that infers that the composite has strong UV blocking efficiency. Furthermore, it was well known that absorption bands of

$ZrO_2$ NPs were not exist at the visible region 400-600 nm; hence it is suggested that the loss of transparency in this visible region (450 nm) were caused only by the light scattering. The transmittance in the UV wave length range was very low indicating that the prepared film could be used as UV-blocking materials. The observed higher transmittance in the near IR region indicates that the prepared nanocomposites could be used as window layer for solar cells as well.

## 3. CONCLUSION

The synthesized functional polymer composite made up of Poly (NVC-co-EMA) and $ZrO_2$ nanocomposites showed high absorption and low transmittance in the UV spectrum. The XRD studies confirm that the Poly (NVC-co-EMA) was synthesized with good compatibility. The optical studies results showed that Poly (NVC-co-EMA) (2%) nanocomposites exhibited a good UV screening effect since their absorption at wavelengths below 350 nm. The optical properties of polymer nanocomposites may open new avenues in UV shielding coating materials.

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