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Synthesis and Characterization of an Infrared-blocking Coating for Sustainability Applications

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Abstract

This study delves into the structural, optical and mechanical properties of polyvinyl alcohol (PVA)-based coatings incorporated with CdS and ZnS nanoparticles at different weight percentage (0 ,4 ,12 and 16) wt%, specifically designed for their infrared (IR) radiation-blocking capabilities. In today's context of increasing demand for effective IR radiation management in applications such as energy-efficient building coatings and thermal control systems, the investigation of these composite coatings is of paramount importance. Accordingly, conducted a systematic study using advanced techniques such as mechanical ,optical and characterization properties.

From the XRD results, pure PVA appears randomly, with no peaks, but when nanoparticles are added, the crystallinity increases clearly. The results of the adhesion strength of the polyvinyl chloride coating without any additives also showed weak adhesion resistance. When grafted with NPs (CdS or ZnS), the resistance gradually increases. .Micro hardness results display ZnS would likely have higher micro hardness

compared to CdS. This is because ZnS has smaller particle size compared to CdS and results of scratch show addition of NPs to PVA can enhanced scratch hardness under 0.5 kg load as a compare with pure PVA. The scratch hardness of the prepared samples also increases with the addition of ZnS and CdS to PVA, which leads to enhanced scratch hardness under a load of 0.5 kg compared to pure PVA. Two PVA/NPs composites, 4% PVA/ZnS and 4% PVA/CdS, were investigated for radiation shielding in the study; the latter demonstrated greater shielding than the former. The PVA/CdS composite has the potential to filter infrared radiation more effectively because of the semiconductor material's ability to absorb and reflect infrared radiation, increasing its overall infrared blocking capacity. Both composites effectively shielded radiation when compared to the atmospheric value.

Keywords: Nano Composites, PVA, ZnS and CdS Semiconductors, Sustainability, Applications.

Introduction

Coatings with the ability to block infrared (IR) radiation have gained significant attention in recent years since their wide-ranging applications in various fields, including aerospace, defense, and energy sectors. These coatings offer superior thermal insulation, camouflage, and

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energy-efficient solutions, among other benefits. Researchers have explored different materials and compositions to develop effective IR-blocking coatings [1],[2]. Two prominent materials that have demonstrated promising results in this regard are polyvinyl alcohol (PVA) and cadmium sulfide (CdS) or zinc sulfide (ZnS) . PVA is a versatile polymer known for its excellent film-forming properties, biocompatibility, and ease of processing. It has been extensively used in various applications, including coatings, adhesives, and packaging materials. CdS and ZnS are wide-bandgap semiconductors that exhibit remarkable optical properties, making them suitable candidates for IR-blocking applications. These materials possess high transparency in the visible region while efficiently absorbing and reflecting IR radiation [3],[4].

Recent advancements in materials science have enabled the development of PVA-based coatings embedded with semiconductor nanoparticles like CdS and ZnS, which exhibit impressive optical and electronic properties, including the ability to block IR radiation. These coatings can potentially revolutionize industries where IR management is essential, such as the construction sector and aerospace applications. However, to effectively harness their IR-blocking capabilities and ensure their durability, a comprehensive understanding of their mechanical behavior is imperative[5].

Numerous research works have examined the mechanical characteristics of PVA-based coatings and composites, concentrating on their ability to block infrared radiation. For example, Johnson et al.'s study [1] examined the mechanical resilience and stress-resistance of PVA/CdS coatings, providing insight into the coating's capacity to preserve its IR-blocking characteristics. Similarly, the mechanical behavior of PVA/ZnS coatings was investigated in a work by Smith and colleagues [2],[6], highlighting the relationship between coating flexibility and nanoparticle dispersion.

This study attempts to clarify the complex link between nanoparticle integration, coating thickness, and mechanical performance using sophisticated characterization techniques, such as nanoindentation, micro hardness testing, and mechanical stress analysis [2],[7],[8]. The study's insights will not only advance our basic knowledge of these materials but also make it easier to adapt their use in real-world applications where both mechanical durability and effective IR blocking are required [9 , 11].

Experimental Part

1. Synthesis of PVA/NPs (CdS or ZnS) thin films

The synthesis of PVA/NPs (CdS or ZnS) thin films involves several steps, first we dissolved PVA powder with different weight fraction(show Table 1 and 2) in 100ml of distilled water to create a PVA solution. After that, NPs (CdS or ZnS) nanoparticles are dispersed in a suitable solvent, such as ethanol or water. We mixed in 100 ml of distilled water. This step aims to achieve a homogeneous mixture of nanoparticles in the liquid phase.

Then combine the PVA solution and NPs (ZnS or CdS) dispersion in the desired ratio (Table 2). The mixture was stirred to ensure complete mixing and dispersion of the NPs within the PVA solution. Stirring with a magnetic stirrer (2 hours) or sonication can be used for this purpose (30 min). We then applied the PVA-NPs mixture onto the desired substrate using a suitable thin film coating method. Some commonly used methods include spin coating, dip coating, spray coating, or doctor blade coating. The choice of method depends on factors such as the substrate material, film thickness requirements, and equipment availability. We used dip coating and casting methods (Depending on the shape of the sample required for examination).

At the end of the process allow the coated substrate to dry in a controlled environment. This step involves removing the solvent from the coating, typically by evaporation. Depending on the solvent used, drying can be achieved by using an oven for 7 hours at 80 °C. Curing may also be necessary to enhance the film's properties, which can be done by subjecting the film to heat or other appropriate treatments.

Table 1: The specifications of the primary materials.

Name	Poly (vinyl alcohol) (PVA)	Cadmium sulfide (CdS)	Zinc sulfide (ZnS)
Molecular formula	[-CH2CHOH-]n	CdS	ZnS
Molecular weight (g/mol)	1,60,000	144.46	97.474
Color	White	Yellow	White
Shape	Powder	Nanoparticles	Nanoparticles
Particle size	-	4 nm	6.5 nm
Supplier	Nashik , india	China	British

Table 2: The weight percent of NPs which added to PVC

PVA (wt%)	NPs (wt%) (CdS or ZnS)
100	0
96	4
88	12
84	16

2. Results and Discussions

2.1 X-Rays Diffraction (XRD) analysis

The prepared samples were characterized by the X-ray diffraction spectra (XRD) as shown in (Figures 1 and 2). In general pure PVA appears randomly and there is broad peak , but when nanoparticles are added, the crystallinity increases gradually. Several factors can influence the crystallinity of PVA when nanoparticles are added. where the size of the nanoparticles can have an impact on the crystallinity of PVA. Smaller nanoparticles generally provide more active sites, promoting the formation of crystalline regions within the polymer matrix.

The XRD patterns of pure and PVA dopped with ZnS NPs samples (4 and 16 wt%) are shown in (Figure 1). The prominent diffraction peaks at [11.5◦], [20◦] [28◦] [29◦] [31◦] [48◦] [53◦] and [58◦] for (331), (200),(220),(311),(222),(400),(420) and (511) planes respectively are the cubic zinc structure of the ZnS . The reason is due to the increase in crystallinity after the addition of NPs to the concentration or loading of ZnS NPs inside the PVA matrix. Higher nanoparticle concentrations can lead to increased nucleation and crystallinity, thus enhancing the overall crystallinity of PVA as shown with the 12 wt% addition [12].

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The XRD patterns for the PVA and CdS in (Figure 2). The crystalline nature of the prepared nanocomposite is attributed to the strong intermolecular interaction between PVA and the NPs (ZnS, CdS). When NPs are introduced into the PVA matrix, they can act as active sites, promoting the formation of ordered crystalline structures within the polymer matrix. The intermolecular interaction between PVA and NPs enhances the crystallinity of PVA, as observed in the XRD patterns. Especially ZnS NPs because its particle size (4 nm) less than CdS NPs (6.5nm)[13].

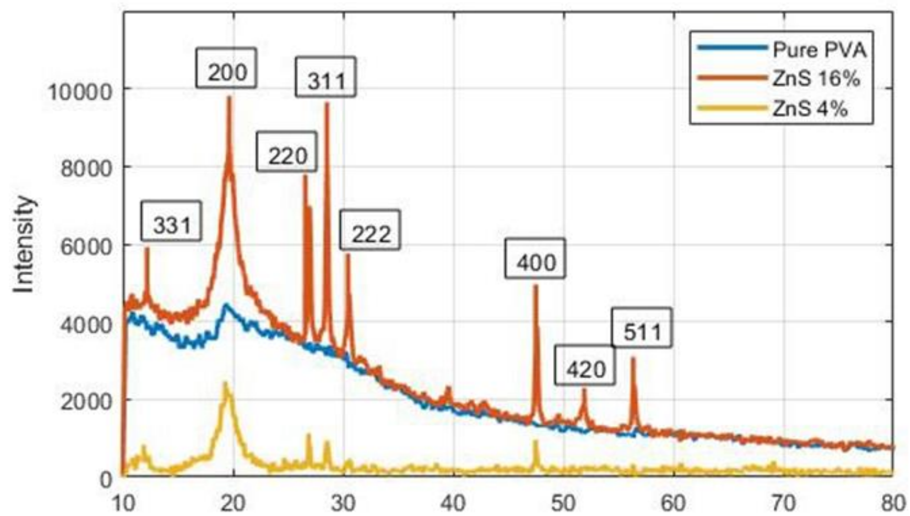


Figure 1 : XRD PVA with 4 and 16wt% ZnS NPs.

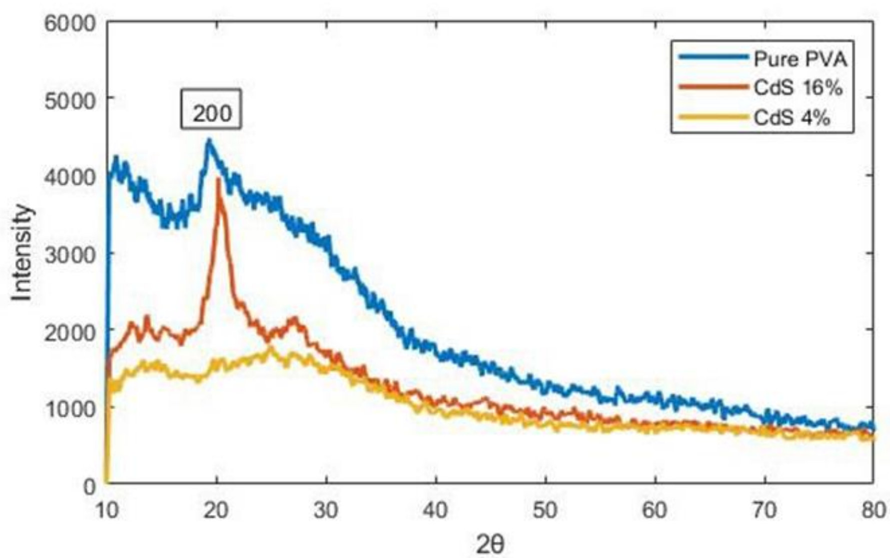


Figure 2 : XRD PVA with 4 and 16wt% ZnS NPs.

Table 3 : crystallite size of pure PVA and PVA/NPs

Sample	Crystallite size (nm)
Pure PVA	16
96 wt% PVA + 4 wt% ZnS	22
88 wt% PVA + 12 wt% ZnS	41
96 wt% PVA + 4 wt% CdS	28
88 wt% PVA + 12 wt% CdS	49

2.2 Shielding Radiation Test

The coating was tested by sheilding radation with the following ratios: 4% PVA/ZnS and 4% PVA/CdS. The value of gamma rays in the atmosphere was (1073). When examining coating made from PVA/ZnS, the radiation value was (1747) , while for coating made from PVA/CdS the value was (1718). The coating made with PVA/CdS showed higher shielding compared to PVA/ZnS. In both cases, the coating showed shielding of radiation compared to the value in the atmosphere.Its has the potential to filter infrared radiation more effectively. This is due to the semiconductor material's ability to both absorb and reflect infrared radiation, which improves the PVA/NPs composite's overall infrared blocking capacity [14].

2.3 Adhesion Strength Test

This test is very important in view point of IR-blocking because it gives indicators about the film integrity, durability,uniformity and the surface finishing . The strong adhesion between the substrate and the coating film maintains the integrity of the IR blocking layer (PVA . Nano composite) on the substrate. Otherwise,if the adhesion is weak , crack may be developed, which leading finally to delaminating or peeling the IR means that the film have enough durability against the exposuring of chemicals, mechanical forces, humidity and the temperatures variations. This test ,also gives an indicator about the thickness variation of the film, thickness uniformity. Irregular thickness can resulted in creating localized areas which have poor IR blocking abilities.

The pull off test was carried out on the prepared samples to evaluate the adhesion strength,as shown in (Figure 3).

(Figure 3 and 4) shows the results of adhesive strength of the coatings. The polyvinyl chloride material was tested without additives (without NPs in pure state), and the result showed a weak adhesive resistance. However, when it was doped with NPs (CdS or ZnS), the resistance gradually increased. The coating was applied to both pure concrete and rubber-infused concrete, fiber, other materials.

When applied to pure concrete initially, the adhesive resistance increased but when the coating was applied to the rubber-infused concrete in different ratios, the adhesive resistance gradually decreased. This indicates that the coating should practically be used on pure concrete without additives to ensure a longer life time. In general PVA with CdS shows higher strength adhesion than PVA with ZnS [15, 20].

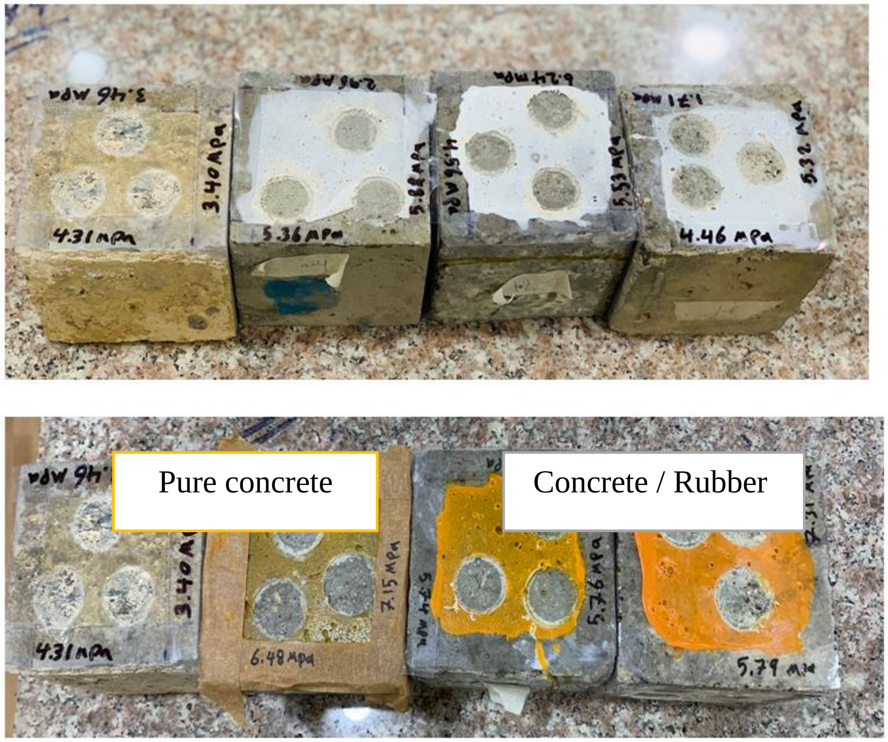


Figure 3: illustrate adhesion strength test for pure PVA and PVA/NPs samples.

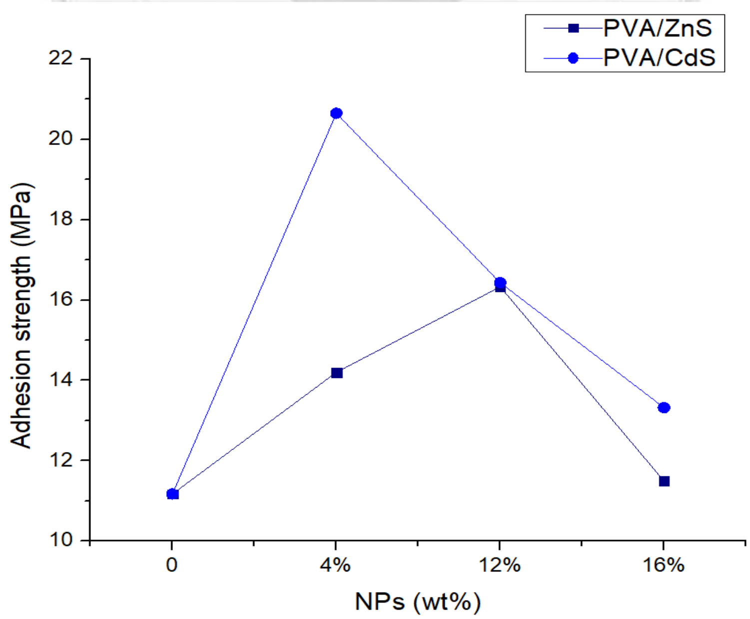


Figure 4 :Adhesion strength values for PVA/NPs (with different ratio).

2.3 Micro hardness Test

The hardness is defined as the resistance of material against surface deformation caused by external load.

(Table 4) shows increment in the micro hardness of the PVA/ZnS coatings from 13.73 HV to 26.44 HV , as well as for PVA/CdS coatings from 8.03 HV to 41.46 HV. ZnS would likely have higher micro hardness compared to CdS. This is because ZnS has smaller particle size compared to CdS.

A higher micro hardness is beneficial for blocking IR radiation. A harder coating is less likely to suffer from damage or wear over time, and it can provide better protection against IR radiation. So, if you're looking to block IR radiation effectively[21]-[23].

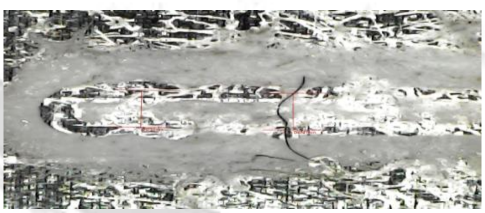
Table 4 : Micro hardness to PVA and PVA/NPS, samples.

NPs (wt%)	Micro hardness (HV) (PVA/ZnS)	Micro hardness (HV) (PVA/CdS)
0	17.4	17.4
4	13.73	8.03
12	17.57	11.41
16	26.44	14.46

2.4 Scratch test

(Table 5) shows the shaps and values of scratch hardness of prepared samples. Addition of ZnS and CdS to PVA can enhanced scratch hardness under 0.5 kg load as a compare with pure PVA. Materials with suitable value of hardness, elastic modules have highe scratch hardness as shown in (Table 5). PVA/ZnS provide better resistance to scratches compared to PVA/Cds due to the higher hardness of zinc sulfide[24 , 26].

Table 5 : scratch hardness of PVA and PVA/NPs,samples

Sample	Shape of Scratch hardness	Scratch hardness value (μm)
Pure PVA		0.0298

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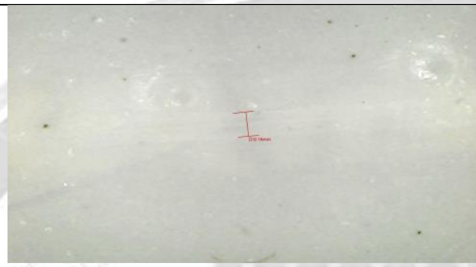
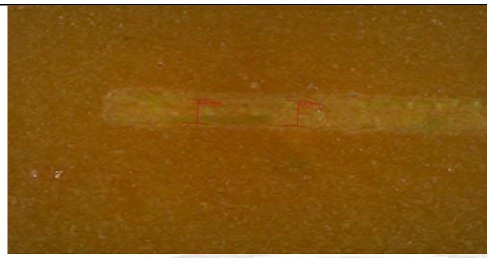
4wt% ZnS		0.086
12wt% ZnS		0.0597
16wt% ZnS		0.0796
4wt% CdS		0.073
12wt% CdS		0.063

16wt% CdS		0.056

Conclusion

According to studies on the mechanical features of coatings that block infrared (IR) radiation, these coatings have qualities that make them promising for use in thermal insulation applications. The results show that mechanical characteristics are important for IR-blocking coating performance. The study emphasizes how crucial it is to choose materials and formulas that strike a balance between mechanical durability and IR-blocking properties. Two PVA/NPs composites, 4% PVA/ZnS and 4% PVA/CdS, were investigated for radiation shielding in the study; the latter demonstrated greater shielding than the former. The PVA/CdS composite has the potential to filter infrared radiation more effectively because of the semiconductor material's ability to absorb and reflect infrared radiation, increasing its overall infrared blocking capacity. Both composites effectively shielded radiation when compared to the atmospheric value. According to the XRD data, pure PVA exhibits no peaks and appears randomly; nevertheless, the addition of nanoparticles obviously boosts the crystallinity. Weak adhesion resistance was also demonstrated by the adhesion strength of the polyvinyl chloride coating in the absence of any additives. The resistance gradually rose when NPs (CdS or ZnS) were grafted. This holds true for the microhardness findings. Additionally, the manufactured samples' scratch hardness.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

[1] N. Baranwal and S. P. Mahulikar, "Review of Infrared signature suppression systems using optical blocking method," Defence Technology, vol. 15, no. 3, pp. 432-439, 2019.

[2] K. Ojha, "Structural and optical properties of PVA doped zinc sulphide thin films," Optik, vol. 127, no. 5, pp. 2586-2589, 2016.

[3] N. Baranwal and S. P. Mahulikar, "Review of Infrared signature suppression systems using optical blocking method," Defence Technology, vol. 15, no. 3, pp. 432-439, 2019.

[4] K. Ojha, "Structural and optical properties of PVA doped zinc sulphide thin films," Optik, vol. 127, no. 5, pp. 2586-2589, 2016.

[5] F. H. Getman, "A STUDY OF THE LEAD ELECTRODE," Journal of the American Chemical Society, vol. 38, no. 4, pp. 792-801, 1916.

[6] A. S. Hasan, A. H. Mousa, and A. R. A. Hussein, "Molecular Dynamics Simulation of SWCNT/PYA in sensors application," in 2022 Muthanna International Conference on Engineering Science and Technology (MICEST), 2022.

[7]J. Koteswararao, S. V. Satyanarayana, G. M. Madhu, and V. Venkatesham, "Estimation of structural and mechanical properties of Cadmium Sulfide/PVA nanocomposite films," Heliyon, vol. 5, no. 6.

[8] M. Othman, A. Bushroa, and W. N. R. Abdullah, "Evaluation techniques and improvements of adhesion strength for TiN coating in tool applications: a review," Journal of Adhesion Science and Technology, vol. 29, no. 7, pp. 569-591, 2015.

[9] M. Kadhim, A. Hasan, M. Akraa, and A. Layla, "Preparation and optimization of heterojunction donor (DLC)–acceptor (SI) as a solar cell by DFT and PLD," Journal of Ovonic Research, vol. 2021, pp. 273-281, 2021.

[10] S. F. A. AL-Abass, A. J. Braihi, and A. Hasan, "Oil spill cleaning up by polymeric sorbents using salt leaching method," in AIP Conference Proceedings, 2023.

[11] T. Arai, H. Fujita, and M. Watanabe, "Evaluation of adhesion strength of thin hard coatings," Thin Solid Films, vol. 154, no. 1-2, pp. 387-401, 1987.

[12] S. K. Jebur, A. J. Braihi, and A. S. Hassan, "Graphene effects on the structural, morphological and optical properties of PEDOT: PSS thin films," Materials Today: Proceedings, vol. 49, pp. 2733-2740, 2022.

[13]S. Sarkar, R. K. Baranwal, C. Biswas, G. Majumdar, and J. Haider, "Optimization of process parameters for electroless Ni–Co–P coating deposition to maximize micro-hardness," Materials Research Express, vol. 6, no. 4, p. 046415, 2019.

[14] J. Svobodová, I. Lysoňková, and M. Krejčí, "Microhardness and Nano-hardness Measurement of Composite Coatings Applied to Aluminium Substrate," Manufacturing Technology, vol. 19, no. 4, pp. 700-705, 2019.

[15] A. Hasan, B. Kadem, M. Akraa, and A. Hassan, "PVA: PEDOT: PSS: carbon based nano-composites for pressure sensor applications," Digest Journal of nanomaterials and biostructures, vol. 15, no. 1, pp. 197-205, 2020.

[16] Y.-G. June, K. I. Jung, M. Choi, T. H. Lee, S. M. Noh, and H. W. Jung, "Effect of urethane crosslinking by blocked isocyanates with pyrazole-based blocking agents on rheological and mechanical performance of clearcoats," Coatings, vol. 10, no. 10, p. 961, 2020.

[17] B. Janani, M. K. Okla, M. A. Abdel-Maksoud, H. AbdElgawad, A. M. Thomas, L. L. Raju, et al., "CuO loaded ZnS nanoflower entrapped on PVA-chitosan matrix for boosted visible light photocatalysis for tetracycline degradation and anti-bacterial application," Journal of Environmental Management, vol. 306, p. 114396, 2022.

[18] S. H. Abud, A. S. Hasan, M. Almaamori, and N. Bayan, "Enhancement the ability to pump crude oil using rubber solutions," in Journal of Physics: Conference Series, 2021.

[19] Y. Khairy, I. Yahia, and H. Elhosiny Ali, "Facile synthesis, structure analysis and optical performance of manganese oxide-doped PVA nanocomposite for optoelectronic and optical cut-off laser devices," Journal of Materials Science: Materials in Electronics, vol. 31, pp. 8072-8085, 2020.

[20] H. Rafeeq, A. Hussain, A. Ambreen, M. Waqas, M. Bilal, and H. M. Iqbal, "Functionalized nanoparticles and their environmental remediation potential: a review," Journal of Nanostructure in Chemistry, vol. 12, no. 6, pp. 1007-1031, 2022.

[21] M. Akraa, A. S. Hasan, and M. J. H. Kadhim, "Spectroscopy characterization of ethylene vinyl acetate degradation by different kinds of accelerated aging," Baghdad Science Journal, vol. 17, no. 3, pp. 0795-.

[22] A. Badawi, G. A. Mersal, A. A. Shaltout, J. Boman, M. Alsawat, and M. A. Amin, "Exploring the structural and optical properties of FeS filled graphene/PVA blend for environmental-friendly applications," Journal of Polymer Research, vol. 28, pp. 1-12, 2021.

[23] A. El-naggar, Z. K. Heiba, M. B. Mohamed, A. Kamal, G. Lakshminarayana, and O. H. Abd-Elkader, "Effect of MnS/ZnS nanocomposite on the structural, linear and nonlinear optical properties of PVA/CMC blended polymer," Optical Materials, vol. 128, p. 112379, 2022.

[24] A. D. Terna, E. E. Elemike, J. I. Mbonu, O. E. Osafile, and R. O. Ezeani, "The future of semiconductors nanoparticles: Synthesis, properties and applications," Materials Science and Engineering: B, vol. 272, p. 115363, 2021.

[25] F. Q. Mohammed, M. S. Edan, A. S. Hasan, and A. J. Haider, "Synthesis and Theoretical Concepts of Boron Nitride Nanowires Grown on Nitrides Stainless Steel Surface by Hybrid Gas Phase Process," in Key Engineering Materials, vol. 886, pp. 97-107, Trans Tech Publications Ltd, 2021.

[26] X. Qian, J. Yin, X. Guo, Y. Yang, Z. Zhu, and J. Lu, "Polymer-inorganic nanocomposites prepared by hydrothermal method: PVA/ZnS, PVA/CdS, preparation and characterization,"

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توليف وتوصيف طلاء يحجب الأشعة تحت الحمراء يدخل في تطبيقات الاستدامة

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الخلاصة

تتناول هذه الدراسة الخواص التركيبية والبصرية والميكانيكية لكحول البولي فينيل الطلاءات المعتمدة على (PVA) والمدمجة مع جسيمات ZnS , CdS النانوية بنسب وزن مختلفة (0,4,14 and 16 wt%) ، مصممة خصيصًا لقدراتها على حجب الإشعاع بالأشعة تحت الحمراء .(IR) في سياق الطلب المتزايد اليوم على الإدارة الفعالة للأشعة تحت الحمراء في تطبيقات مثل طلاءات المباني الموفرة للطاقة وأنظمة التحكم الحراري، فإن دراسة هذه الطلاءات المركبة لها أهمية قصوى. وبناء على ذلك، أجريت دراسة منهجية باستخدام تقنيات متقدمة مثل الخصائص الميكانيكية والبصرية والتوصيفية.

من نتائج XRD ، يظهر PVA نقي بشكل عشوائي، مع عدم وجود قمم، ولكن عند إضافة الجسيمات النانوية، تزداد التبلور بشكل واضح. كما أظهرت نتائج قوة التصاق طلاء البولي فينيل كلوريد بدون أي إضافات ضعف مقاومة الالتصاق. عند تطعيمها بـ NPs CdS أوZnS ، تزداد المقاومة تدريجيًا. تظهر نتائج الصلابة الدقيقة أنه من المحتمل أن يكون لـ ZnS صلابة دقيقة أعلى مقارنة بالأقراص المدمجة. وذلك لأن ZnS له حجم جسيمات أصغر مقارنة بـ CdS وتظهر نتائج الخدش أن إضافة NPs إلى PVA يمكن أن يعزز صلابة الخدش تحت حمل 0.5 كجم مقارنة مع PVA النقي. كما تزداد صلابة الخدش للعينات المحضرة مع إضافة ZnS وCdS إلى PVA، مما يؤدي إلى تعزيز صلابة الخدش تحت حمل يبلغ 0.5 كجم مقارنةً بـ PVA النقي. تمت دراسة نسبتين من PVA/NPs، PVA/ZnS 4% و4% PVA/CdS، للوقاية من الإشعاع في الدراسة؛ أظهر الأخير حماية أكبر من الأول. يتمتع مركب PVA/CdS بالقدرة على تصفية الأشعة تحت الحمراء بشكل أكثر فعالية بسبب قدرة المادة شبه الموصلة على امتصاص وعكس الأشعة تحت الحمراء، مما يزيد من قدرتها الإجمالية على حجب الأشعة تحت الحمراء. كلا المركبين يحميان الإشعاع بشكل فعال بالمقارنة مع قيمة الاشعاع في الجو.

الكلمات الدالة: مركبات النانو، PVA، ZnS وCdS، أشباه الموصلات، تطبيقات الاستدامة.