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A Study on Structural, Mechanical and Thermal Properties of Polymer Composites of Poly(vinyl alcohol) with Inorganic Material

Gulfam Nasar, Muhammad Saleem Khan, Uzma Khalil*

Summary: In this paper we have tried to find the relationship of thermal and mechanical properties i. e. thermal conductivity, tensile strength and Young's Modulus of the composite material. Two systems were selected; poly(vinyl alcohol)/sodium sulphate composite, and poly(vinyl alcohol)/lithium sulphate composite. Various concentrations of these salts were used to make composites of poly(vinyl alcohol). Films were grown, dried at room temperature and were subjected to mechanical, structural and thermal characterization. Thermal conductivity was determined at room temperature using polyethylene, silicon and quartz as reference. It was found out that the thermal conductivity of both the systems is highly dependent on the nature and the concentration of added salt in the polymeric composite. Thermal conductivity of the poly vinyl alcohol/ sodium sulphate composite, and poly vinyl alcohol/lithium sulphate composite, decreased with concentration of the salts in the polymer composite. These composites were also analyzed by XRD. Observed roperties were explained on the bases of their structure. Machenical properties such as tensile strength and Young's Modulus were also found out to be a function of the compostion of the composite

Keywords: lithium sulphate; poly(vinyl alcohol); PVA; sodium sulphate; thermal conductivity

Introduction

Composite materials may be defined as materials made up of two or more components forming two or more phases. Such materials must be heterogeneous at least on a microscopic scale. During the past few decades there has been a rapidly increasing search for strong, stiff, abrasion/impact resistant and corrosion free structural materials with low densities.[1] Properties of composite materials greatly depend on the nature of the matrix and the filler, their compatibility, nature size of the combining units and their relative properties. In this study, we have taken into account a comparison of thermal and mechanical properties of polymeric composite materials.[2–4]

Most techniques to measure the thermal conductivity rely on bulk samples and are not applicable to films. The extrapolation from a bulk measurement to the film can be misleading.[5,6] Material properties should be best measured in a film as it is processed in a final application. So is is important to measure the properties of a material in form of thin film. For thin films steady-state and pulse techniques have been developed.[7]

In the present study a Quick thermal conductivity meter (QTM-500 manufactured by Kyoto Electronics Manufacturing Company Ltd. Japan) was used. QTM works on 'hot wire method' and detects thermal conductivity of a sample on the principle of change of thermal conductivity with change in temperature as a function of

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National Center of Excellence in Physical Chemistry,
University of Peshawar, Peshawar 25000, Pakistan
E-mail: gulfamnasar@yahoo.com

electric current. The use of such thermal conductivity meter for measurement of thermal conductivity of polymers and polymer composites is very limited. It has never been used before for the study of thermal conductivities of polymeric films. So, through this paper we report for the first time the use of QTM for the system under investigation during our research.

The presence of any second phase (dispersed phase in the form of a polymer or a filler) in a polymer matrix (dispersion medium) affects the mechanical properties of the mixture (blends or composites) depending on the relative concentration of the two phases, nature of the disperse phase, surface characteristics, distribution of one phase in another, domain size and shape, adhesion between two phases, size of the particles, surface area and degree of compatibility, in particular.[8] The mechanical properties change by varying the composition of components of a composite material as well as with the applied force. In our study, the mechanical properties were determined from tensile properties of the prepared samples.

Experimental Part

Chemicals Used

A customary polymer poly(vinyl alcohol), PVA was used in this investigation. PVA with molecular weight of approximately 125,000 g/mol ($T_m = 270\,^\circ C$ and $T_g = 85\,^\circ C$, acetoxy groups 2.5%) was obtained from BDH chemical Ltd England. Research grade sodium sulphate was obtained from BDH Chemical Limited England. Research grade lithium sulphate was obtained from Merk, Germany.

Preparation of Stock Solutions

Stock solutions of 1 M sodium sulphate and 1 M lithium sulphate were prepared which were used to prepare composites of different compositions. Weighing of all chemicals and polymer was done on AND HR200 type top loading balance.

Preparation of Polymer Composite Films

Individual stock solutions of the salts were prepared from one primary stock solution by dilution. 3.0 g of solid PVA was added in each diluted solution. Thus 0.2, 0.4, 0.6, 0.8 and 1.0 wt % salt concentrations were prepared. The components were dissolved using a magnetic stirrer with hot plate by simultaneous heating and stirring for 12 hours at 70 °C. Solutions of the composites were transferred to Petri dishes and films were prepared by solvent evaporation method. Prepared films were annealed at 30 °C for 6 hours, then vacuum dried, removed and cut into specimens of appropriate sizes and shape for the characterization tests.

Characterization

Thermal conductivity of polymer composites varies depending upon the nature and composition of the added materials to the pure polymer. A study on thermal conductivity was carried out to investigate the effect of concentration of the inorganic material on thermal conductivity in a composite. Thermal conductivity was measured using Quick Thermal conductivity Meter, QTM-500 (Model SOFT-QTM 5EW) manufactured by Kyoto Electronics Manufacturing Co. Ltd Japan. Rectangular pieces of 100 mm x 50 mm sizes of samples were used. Thermal conductivity of each sample was measured using three slabs of different materials (polyethylene, silicon and quartz) of known value. Thermal conductivity values of the reference slabs are given in Table 1.

The samples of different compositions of each polymer composite were placed hor-

Table 1.
Standard thermal Conductivities of Reference Slabs.

S No.	Reference Material	Thermal Conductivity W/m K	
		Measured value	Reported value
1	Polyethylene	0.0935	0.10–0.21
2	Silicon	0.2385	0.22–0.26
3	Quartz	1.4156	1.39–1.49

izontally between thermocouple and the reference slab one by one, allowing full contact with thermocouple on one side and with reference slab on the other side. Three readings were taken with respect to each reference slab. Each reading took about 45 minutes to reach the steady state. Precision and reproducibility of the instrument is 5% and 8% respectively per each reference slab. Average values of the thermal conductivity for each sample were calculated. The analysis was performed at 30 °C.

The samples were exposed to stress-strain experiments. This gives the chance to check orientation and anisotropic behavior of the samples. Testometric Universal Testing Machine M350/500 manufactured by Testometric UK was used for analysis. Films of pure polymer and of selected compositions of the polymer composites were cut into standard dumbbell shapes having sample length 50 mm and gauge length 15 mm. The analysis was performed at room temperature with crosshead speed of 5 mm/min. For high accuracy and precision, a sensitive load cell of 100 kg capacity was used.

Results and Discussion

The thermal conductivity, λ, is the quantity of heat transmitted, due to unit temperature gradient, in unit time under steady state conditions in a direction normal to a surface of unit area, when the heat transfer is only dependent on the temperature gradient.[9] Thermal conductivity is measured in W m^{-1} K^{-1}.[10] The thermal conductivity of the pure PVA changes strongly with addition of sodium sulphate and lithium sulphate. Hence thermal conductivity of composite materials depends on the matrix material and the dispersed substance.

PVA/Sodium Sulphate Composite System

Figure 1 shows the measured values of thermal conductivities of various samples of PVA/sodium sulphate composites. It is clear from Figure 1 that thermal conductivity of the PVA/sodium sulphate system decreases with concentration (wt %) of sodium sulphate. This is in accordance with the previously conducted study on a similar system.[11]

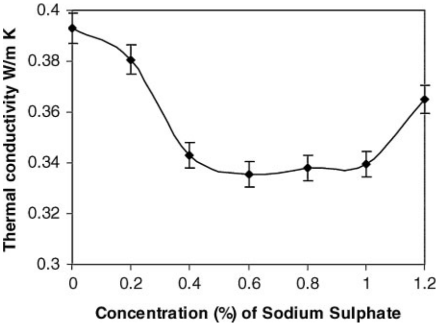

Figure 1.
Plot of the thermal conductivity versus the sodium sulphate content [% w/w].

This phenomenon is due to the fact that a decrease in the thermal conductivity is mainly due to the a deviation from the semi-crystalline structure of the pure PVA.[12] Phonons passing sufficiently in number and rapidly through the crystalline structure, break down the crystal lattice to an amorphous structure and cause scattering of the phonons to irregular paths in different directions. The result is an overall decrease in thermal conductivity at the surface and in the semi-crystalline bulk. An XRD study of the same system confirms this explanation as shown by Figure 2.

Morphology of the added salt also has a role in lowering the thermal conductivity of the composite. It is notable that thermal conductivity reaches the minimum threshold value and then increases, but does not exceed that of pure polymeric film. An increase in thermal conductivity at higher concentration of salt is due to the thermal conduction of the crystalline salt and an overcompensation in the composite.

PVA/Lithium Sulphate Composite System

Like PVA/sodium sulphate composite, this composite also loses thermal conductivity with an increase in the salt concentration.

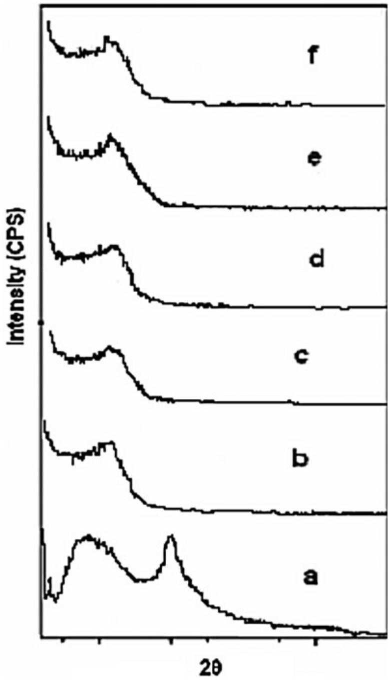

Figure 2.
X-Ray Diffraction Pattern of PVA and sodium sulphate (a) 0 wt% (pure PVA) (b) 0.2 wt% (c) 0.4 wt% (d) 0.6 wt% (e) 0.8 wt% (f) 1.0 wt%.

This is due to the fact that both the salts have similar chemical nature and behaviour. The results of thermal conductivities in PVA/lithium sulphate composites are shown in Figure 3.

The trend of the thermal conductivity shows that both the salts have a comparable impact on thermal conductivity of the composites. The replacement of crystalline phase in the polymer by amorphous structure decreases the thermal conductivity of the composite. The increase in the thermal conductiviy at salt concentration higher than 0.8% can be explained by an overcompensation by the composite material as an effect of inorganic salt beyond the threshold value. The results are confirmed by XRD as shown in Figure 4. Similar behaviour was reported in earlier studies using similar kind of filler in a different polymer matrix.[13]

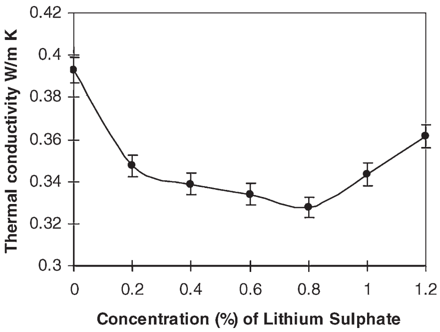

Figure 3.
Plot of the thermal conductivity versus the lithium sulphate content [% w/w].

Tensile Properties of PVA/Na_2SO_4 Composites

Tensile Strength

Tensile strength is the ability of a material to withstand tensile loads without rupture when the material is under tension. The tensile strength of PVA/sodium sulphate composite as a function of wt % sodium sulphate contents has been plotted in Figure 5. The tensile strength decreases

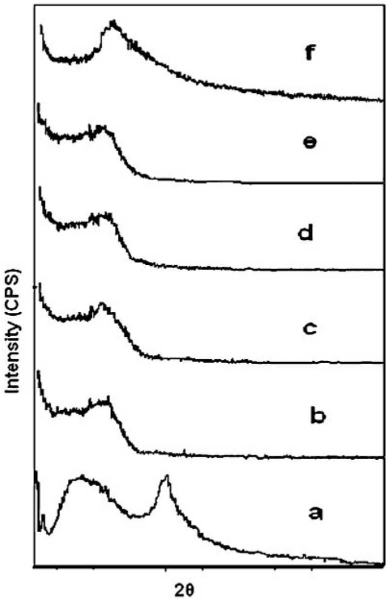

Figure 4.
X-Ray Diffraction patterns of PVA and lithium sulphate (a) 0 wt% (b) 0.2 wt% (c) 0.4 wt% (d) 0.6 wt% (e) 0.8 wt% (f) 1.0 wt%.

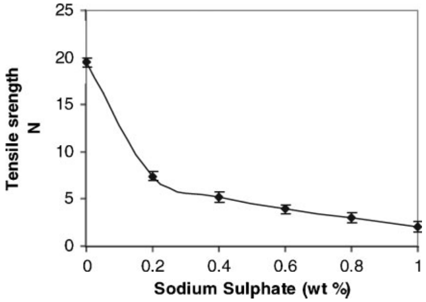

Figure 5.
Variation in Tensile strength for PVA/Na_2SO_4 composite with wt % of sodium sulphate.

with increasing sodium sulphate content. This again is caused by a decrease of the polymer crystallinity. The physical interactions between PVA and Na_2SO_4 weaken the lattice strength of PVA.

Young's Modulus

The tensile or Young's modulus, is a measure of the stiffness of a material. In the present experiments the tensile modulus was measured at very low strain where the stress-strain curve shows maximum linearity. This behavior is associated with the intermolecular (interchenar) interactions. The Young's Modulus drops with addition of salt at lower concentration, but increases at higher concentration due to an interaction between the components of the composite. The salt particles fit in the spaces between the polymer matrix, making it less elastic and more rigid at high salt concentrations as shown in Figure 6. The tensile modulus of the PVA/ sodium sulphate composite as a function of the sodium sulphate content has been plotted in Figure 6.

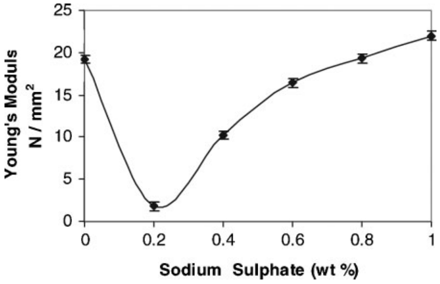

Figure 6.
Variation in Young's modulus for PVA/Na_2SO_4 composite with the amount of sodium sulphate in the composite.

Tensile Properties of PVA/Li_2SO_4 Composites

Tensile Strength

Figure 7 shows the variation in tensile strength with increasing amount of lithium sulphate. The tensile strength of the system decreases significantly at low concentration of sodium sulphate, but increases at concentrations higher than 0.2% (w/w). This is due to the accumulation of the salt in the spaces between matrix polymer coils compensating the loss of strength at lower concentration. Thus the composite shows lesser drop in the tensile strength as compared to that of the PVA/sodium sulphate composite.

Young's Modulus

The Young's modulus of PVA/lithium sulphate composites as a function of wt % sodium sulphate contents has been plotted in Figure 8. The value of Young's modulus of multi-component systems usually follows a rising trend with addition of a stiffer component almost regardless of the quality of adhesion between the components of the composite. Unlike that of the sodium sulphate composite, here the value of Young's modulus increases slightly at a lower concentration, but then increases abruptly at a higher salt concentration. This is because, at a lower concentration, the

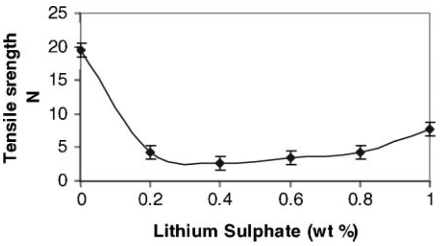

Figure 7.
Variation in tensile strength for PVA/Li_2SO_4 composite with the amount of lithium sulphate in the PVA/lithium sulphate composite.

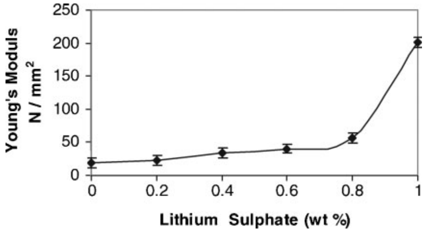

Figure 8.
Variation in Young's modulus curve for PVA/lithium sulphate composite film with wt % change of lithium sulphate.

distance between ions is greater while at a higher concentration interaction between ions increases due to decreasing inter-ionic distance. This increases the strength of the composite. The same phenomenon is found in a different way, however, in case of the sodium sulphate composite at even lower concentration, see Figure 6. This is due to larger inter-ionic interaction at lower concentration and a higher reactivity of the sodium ion towards anions as compared to lithium ion in the PVA/lithium sulphate composite.

Conclusion

PVA/ sodium sulphate and PVA/lithium sulphate composites up to 1% (w/w) of salt content were prepared and thin films were produced by solvent casting. These thin films were characterized concerning thier thermal conductivity, mechanical properties and structural morphology. Thermal conductivity of PVA/sodium sulphate composite and PVA/lithium sulphate composite is less at higher salt concentration in the composite. This makes these composites possible candidates as thermal insulator at a higher concentration of the salt.

PVA/sodium sulphate composite and PVA/lithium sulphate composite show a higher Young's Modulus with higher concentration of the inorganic salt in the composite. This shows a higher compatibility of the components of the composites. Furthermore, both the composites lose their tensile strength with increasing salts concentration in the composite, thus resulting in a decrease in the elastic behaviour of the polymer.

[1] M. Fellah, A. Tounsi, K. H. Amara, E. A. A. Bedia, *Theoretical and Applied Fracture Mechanics* **2007**, *48*, 32.
[2] M. Hu, D. Yu, J. Wei, *Polymer Testing* **2007**, *26*, 333.
[3] U. Gubler, M. Raunhardt, A. Stump, *Thin Solid Films* **2006**, *515*, 1737.
[4] Callister, William "Appendix B", *Materials Science and Engineering - An Introduction*, John Wiley& Sons: INC, **2003**.
[5] C. Lambropoulos, M. R. Jolly, C. A. Amsden, S. E. Gilman, M. J. Sinicropi, D. Diakomihalis, S. D. Jacobs, *J. Appl. Phys.* **1989**, *66*, 4230.
[6] A. J. Griffin, F. R. Brotzen, P. J. Loos, *Journal of Appied Physics*. **1994**, *75*, 3761.
[7] U. Gubler, M. Raunhardt, A. Stump, *Thin Solid Films* **2006**, *515*, 1737.
[8] T. Köhler, F. Vollrath, *Journal of Experimental Zoology* **1995**, *271*, 1–17.
[9] D. R. Lide, *Chemical Rubber Company Handbook of chemistry and physics*; CRC Press, Boca Raton: Florida 1998.
[10] G. W. C. Kaye, T. H. Laby, *Tables of physical and chemical constants*, Longman, London 1993.
[11] W. B. Lui, J. Peng, *Journal of Cellular Plastics* **2004**, *40*, 445.
[12] J.-C. Ǵeminarda, D. H. Bouraya, H. Gayvallet, *Europian Physics*. **2005**, *48*, 509.
[13] G. W. Lee, M. Park, J. Kim, J. I. Lee, H. G. Yoon, *Composites: Part A* **2006**, *37*, 727.