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The Thermal Degradation Kinetics and Morphology of Poly(vinyl butyral) Cast Films Prepared Using Different Organic Solvents

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Abstract. Polyvinyl butyral (PVB) films are highly promising materials as they combine interesting thermal and structural morphology properties and in many cases coating viability. However, the polymerization ability of PVB films through solvent casting method using different solvents is fundamentally not well understood. In this rational, the present study demonstrates the use of Isopropanol, ethanol, methanol, and acetic acid for the development of high quality PVB films. The resulting acetic acid-based PVB film exhibits moderated thermal stability with smooth surface morphology which is an important factor in coating applications. On the other hand, ethanol-based PVB film achieves higher thermal stability relative to all other PVB films with some structural defects attributed to less impurities in the solvents. This study will pave the development of high performance PVB cast films.

INTRODUCTION

Polyvinyl butyral (PVB) is an amorphous thermoplastic, which results from polyvinyl alcohol and butyraldehyde reaction in acidic medium¹. The different groups are responsible for the physical and chemical properties of the polymer, including adhesiveness and the viscoelasticity². PVB is used for many applications such as laminated safety glass, paint, adhesive, primers binders, and etc³. It has the potential of being used as a constituent part of a composite while addressing issues of applications for many industries. Solvent casting method involves the dissolution of a polymer in a suitable solvent and evaporating the solvent to obtain a high-quality film⁴. Studies revealed that PVB is soluble in polar solvents such as acetic acid and many hydrocarbons⁵. Zhang X and his colleagues prepared an alcohol-soluble PVB, where by inexpensive conditions were followed by understanding the molecular structure⁶. However, this study reports no results or discuss the effect of thermal processing of the film.

The thermal properties of polymeric materials are important because the performance is related to the overall application⁷. The thermal properties of neat PVB (without any additives) is rarely reported. The degradation of PVB is influenced by the different groups in the polymeric structure consequently its physical properties are affected⁸. Fernandez et al⁹, reported the synthesis of PVB in homogeneous phases and their thermal properties in N-methyl-2-pyrrolidone. It was concluded that the hydroxyl group content affects the thermal stability and a direct proportionality with the VA contents was observed. However, little has been reported in the literature concerning the influence of different solvents and their thermal analysis of PVB. The present work investigates the influence on thermal stability when using different organic solvents; ethanol, methanol, isopropanol and the acetic acid to dissolve PVB.

EXPERIMENTAL

Materials

PVB and the solvents (methanol, ethanol and isopropanol) were purchased from Sigma Aldrich.

Preparation of cast films

0.5g of PVB was dissolved in 10ml of each solvent. A stirrer was used at 100rpm, for 2 hours for each reaction at room temperature. The solution was poured into a solid molded polypropylene polymer and left to dry under air for 48 hours.

Characterization

Melting point

The melting point was measured using the Stuart SMP20 digital apparatus with an electrical supply of 230V, 50Hz, 75W and 20°C per minute to plateau, variable between 1 and 10°C per minute to melt.

DSC

The DSC-Q2000 instrument (TA instruments) under nitrogen atmosphere using approximately 6mg of the film samples were investigated by initially heating 10°C/min to 300°C and cooling 300°C to -65°C glass temperature of all the samples of PVB prepared in different solvents was studied.

TGA

The TGA Q500 (TA instrument) was used at a heating rate of 10°C under nitrogen, from room temperature to 900°C. Samples were approximately 10mg, the weight loss and the derivative weight loss were graphically presented.

FTIR

Attenuated total reflectance Fourier-transform infrared spectra (ATR-FTIR) spectroscopy with a Perkin-Elmer Spectrum 100 spectrometer (USA) in the range of 600 to 4000 cm⁻¹.

SEM

The morphological analyses of the cast films were carried out by field-emission scanning electron microscopy (FESEM; Zeiss). The samples were sputter coated with chromium before imaging at an acceleration voltage of 3kV.

RESULTS AND DISCUSSION

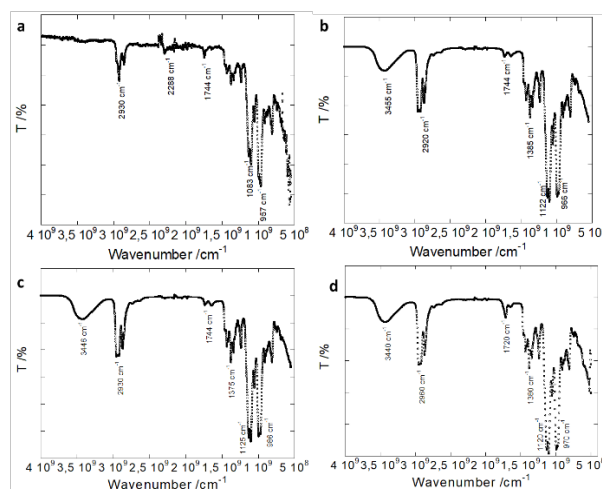
The physical properties of PVB films are shown in TABLE 1, the melting point, thickness and the appearance of the resulted cast films. The physical properties show very little difference between the films. The melting point of the films was found to be on average 137.7°C which corresponds to the neat PVB powder as reported in literature. Methanol and acetic acid have clear optical appearance which could be due to the high polarity. The thicknesses of the films vary due to the differences in their volatile behaviour and the boiling point.

TABLE 1. The physical properties of PVB prepared in different solvents

Cast films	Melting point (°C)	Thickness (μm)	Appearance
PVB-Methanol	129.9 \pm 2.623 – 146.7 \pm 3.047	92.7 \pm 0.005	Clear
PVB-Isopropanol	146.6 \pm 2.709 – 166.9 \pm 2.669	94.7 \pm 0.005	Clear/yellowish
PVB-Ethanol	131.2 \pm 1.654 -156.4 \pm 2.701	53.3 \pm 0.006	Clear/white edges
PVB-Acetic acid	143.0 \pm 1.960 – 166.5 \pm 1.430	75.7 \pm 0.005	clear

FTIR Spectroscopy

The FTIR Spectrum of cast films using ethanol, methanol, isopropanol and acetic acid are shown in FIGURE 1. Both ethanol and Isopropanol are characterized by a broad peak at about 3446 cm^{-1} and 3455 cm^{-1} , respectively, is due to the presence of the stretching vibrations of the –OH group. The broad peak is not visible in methanol spectra due to the alcohol having some acidity slightly higher than water when compared to the ethanol and isopropanol. On the other hand, the absorption of peaks at 2930 cm^{-1} , 2920 cm^{-1} , 2930 cm^{-1} and 2960 cm^{-1} for methanol, isopropanol, ethanol and acetic acid respectively, this peaks are attributed to the –CH bending vibrations. A small doublet peak at 1744 cm^{-1} is seen for the different alcohol solvent and 1720 cm^{-1} for the acetic acid from the –COO group. The –COC group is visible at 1083 cm^{-1} , 1122 cm^{-1} , 1125 cm^{-1} and 1120 cm^{-1} for the solvents, with methanol at a significantly lesser absorption.

**FIGURE 1.** FTIR spectra of PVB in (a) Methanol (b) Isopropanol (c) ethanol and (d) acetic acid

The spectrums show typical peaks attributed to PVA, plus absorptions arising from the presence of acetyl groups between 1083 and 1125 cm^{-1} . The small band at 1744 cm^{-1} appears because of the acetate group. PVB shows no difference by the different alcohol for hydroxylation in to its solvated form. Ethanol and Isopropanol seems to behaving in a similar way and the methanol is odd seen with the band at 2288 cm^{-1} . The reactivity is higher than primary or secondary alcohol which is attributed to the odd nature of methanol. The acid has a small peak that appears at about 1720 cm^{-1} which is the absorption peak of the carbonyl group and is different from the PVB alcohols films. The different solvent has little almost too non-significant change to the chemical composition of PVB. Polar solvents are seen to increase dispersion resulting in more thermodynamically stable structures.

DSC

PVB is amorphous and displays an easily observable glass transition. While we do not get a significant change in the T_g proves shows that the film casting does not alter the VA content. The glass transition of the polymer is seen to be at 67°C for all the solvents and a no significant change is seen with the solvents. The higher the hydroxyl groups result

in high hydrogen bonding which could be the reason why the acidic solvent has a higher T_g compared to the other polar solvents.

TGA

The TG curves show ethanol to have good thermal stability, followed by the methanol, isopropanol and the acetic acid respectively. The degradation of PVB takes place in a single step at 400°C an intense peak is seen for all the solvents. Ethanol has a shoulder on the peak and this is attributed to the small amount of cross-linked and cyclic compounds above 400°C. Major mass loss is due to the decomposition of the polymer chain¹⁰. The hydroxyl groups have a huge effect on the stability of PVB¹¹. The decomposition of PVB takes place in one step when the percentage of VA unit is less than 80%, and PVB starts to decompose at 280°C with a weight loss between 80% and 90% at 480°C. The cast film with acid is less thermally stable when compared to the different alcohols which could be due to the structural order in polar solvents resulting in weak ionic bonding.

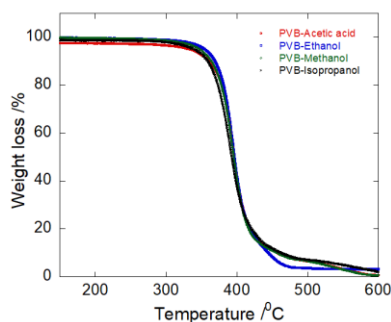


FIGURE 2. The TG curves of the PVB films prepared in different solvent.

The volatility of water is very minimal with a broad small peak, which is due to the volatile solvents used for the cast films.

TGA kinetics

TABLE 2 represents the slope (E_a) of the curve for cast films in methanol, isopropanol, ethanol and acetic acid respectively. It is seen that the film cast using acetic acid has lower activation energy which shows the required energy to propagate the reaction is less resulting in less thermal stability. Films of isopropanol and ethanol are -22,03 and -24.98 kJ/mol and prove to have better thermal stability when compared to the methanol -28.12 and acetic acid -31.17 kJ/mol. The different solvents affect the thermal degradation of the film which is attributed to the polarity of solvents. The data correlates with the weight loss TGA data in Appendix A, which shows that films prepared from ethanol and isopropanol have higher thermal stability than films prepared from methanol and acetic acid attributed to the lower activation energy of the reaction. The results suggest that the solvents used to prepare cast films affect the thermal stability of the end product.

TABLE 2. Activation energy of film of PVB prepared in different solvents.

Films	Activation energy (kJ/mol)
PVB-Methanol	- 28.12
PVB-Isopropanol	- 22.03
PVB-Ethanol	-24.98
PVB-Acetic acid	-31.17

Morphology

The morphological micrographs show that the surface of the films is different with the different solvents. PVB film made from methanol forms some sort of droplets on the surface of the film which is attributed to the volatile nature

of the alcohol. PVB film made from Isopropanol solvent has a consistent surface that is homogenous and shows no defects. A fibrous needle-like structure and roughness is as seen with films made from isopropanol and ethanol. PVB film made from ethanol has a more textured surface which is attributed to the reaction mechanism of the primary alcohol with the polymer. PVB cast film made from acetic acid has a somewhat smooth surface with minor defects. Polymer chains have less energy available to form ordered structures throughout the surface. The surface structures can also be influenced by solvent effects and environmental conditions. The hydroxyl concentration after the solvent has evaporated affect the formation of the morphology.

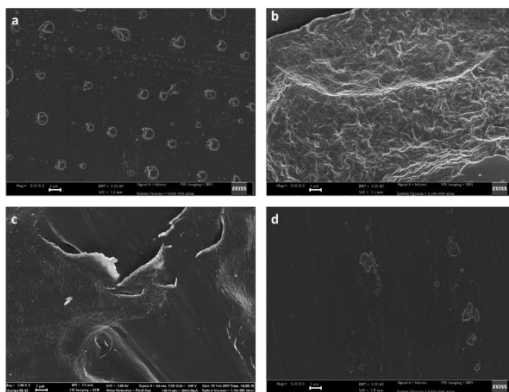


FIGURE 3. The SEM micrographs of PVB cast films with the different solvents (a) methanol (b) Isopropanol (c) ethanol and (d) acetic acid

CONCLUSION

The paper presents the thermal properties of PVB prepared in different solvents by the casting process and the reaction mechanism of the hydrolysis reaction. The chemical composition was not affected by the dissolution of the PVB in the four solvents utilized. The physical properties changes with using different solvents for making films. The surface morphology is affected differently with the use of the different solvents. PVB films and sheets can be utilized in different end-user industries thus understanding the mechanism and thermal stability is crucial. The paper shows a variety of solvents suitable with PVB for a range of applications in the coating industry.

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REFERENCES

1. H. E. Assender, A. H. Windle, *Pol* **39** (18), 4295-4302 (1998).
2. C. E. Carraher, "Polymer Structure (Morphology)," in *Introduction to polymer chemistry*, edited by CRC press (Taylor and Francis Group, 6000 Broken Sound Parkway NW 2017), pp. 27-53.
3. B. Wade, *Encyclopedia of Polymer Science and Technology*, 1-22 (2002).
4. H. Gliemann, A. T. Almeida, D. F. S. Petri and D. Schimmel, *Sur. Inter. Anal.* **39** (1), 1-8 (2007).
5. P. Anbukarasu, D. Sauvageau and A. Elias, *Scie. Rep.* **5**, 17884 (2015).
6. X. H. Zhang, G. L. Yang, J. Q. Hu and C. Y. Zhang, *Adv. Mater. Res* **14**, 1831-1835 (2013).
7. X. Y. Zhao and H. J. Liu, *Pol. Inter* **59** (5), 597-606, (2010).
8. M. K. Barkht, *J. Sci. Ind. Res.* **26**, 35-40 (1983).
9. M. Fernandez and P. Hoces, *J. App. Pol. Scie.* **102** (5), 5007-5017, (2006).
10. J. H. Flynn and L. A. Wall, *Polym. Lett* **4**, 323, (1966).
11. M. Sônego, L.C. Costa, and J.D. Ambrósio. *Pol* **25** (2), 175-180 (2015).