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BIOPOLYMERS BASED ADHESIVES FOR VARIOUS ADHERENTS USING CASEIN /PVA

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ABSTRACT

Novel biopolymer based adhesives were proposed in the present work. It describes the evaluation and analysis of PVA/Casein blend adhesive for the joints of metal to metal, metal to plastic, plastic to plastics. Various combinations of PVA/Casein were prepared. The prepared adhesives were applied to make joints between metal to metal, metal to plastic, plastic to plastic and observed the properties. The adhesives were characterized by FTIR spectroscopy, TGA analysis , DSC and adhesion strength and retention of properties in various mediums were tested. It is found to give promising results with the given adherends.

Keywords: Adhesives, PVA , Casein , adhesion strength, biopolymers etc.

INTRODUCTION:

Casein is the dominant protein group in bovine milk and is the major functional contributor to a family of dairy ingredients which are used ubiquitously in the food industry. The caseins are nature-designed to be dispersed in an aqueous solvent, carry relatively large quantities of calcium and calcium phosphate and still maintain a low viscosity. Casein based materials have been developed due to their particular chemical properties, which provide it a wide range of applications. It is highly soluble in acid solution being a weak base due to the presence of amine groups. [1] At low pH values, the amine groups are positively charged due to protonation, so Casein can be a water-soluble cationic polyelectrolyte. When the pH increases above 6, the amine groups of Casein residues are deprotonated and the biopolymer loses its charge leading to an insoluble polymer [2].

Polyvinyl alcohol (PVA) is a vinyl polymer interconnected by carbon–carbon linkage. It is water-soluble and biodegradable. It also possesses high biocompatibility and is capable of self-crosslinking because of hydroxyl groups present on side chains [3]. Polyvinyl alcohol/Casein based hydrogels blends have high blood compatibility [4] and are good candidates for use as matrices for the controlled delivery of drugs [5]. Koyano et al. reported that PVA/CS hydrogels blended in an autoclave without the use of crosslinkers such as glutaraldehyde or paraformaldehyde exhibited high attachment to and promoted growth of cultured fibroblast cells depending on the

CS content [6]. Yang et al. used a combinational method to crosslink the PVA/CS hydrogel membrane, which significantly improved its swelling, thermo mechanical stability, anti-bacterial properties, and decreased water evaporation [7].

In the current study PVA/ Casein blends were prepared and used for adhesive application are metal to metal, plastics to plastic and metal to plastics joints. Strength of the joints was determined and also the retention of properties in various environments was studied. FTIR, DSC and TGA were conducted for characterization of the blend.

EXPERIMENTAL :

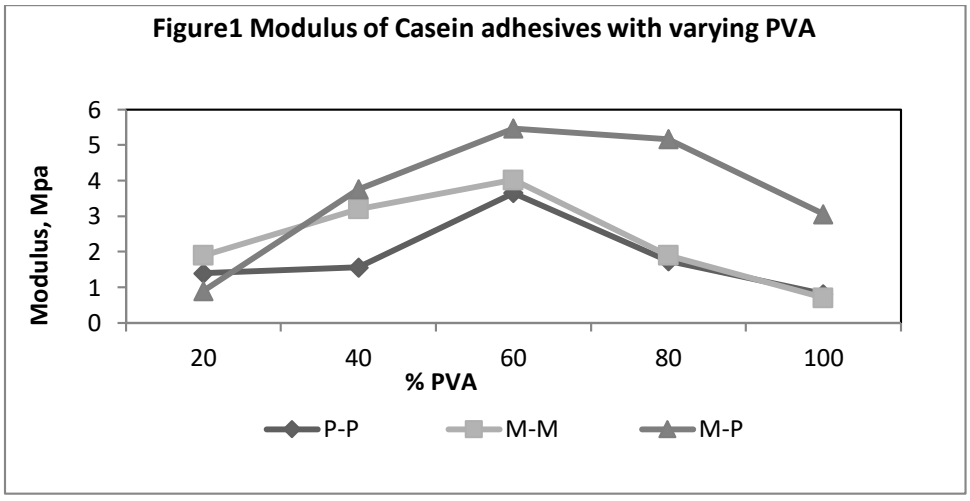
Materials Used:

Polyvinyl alcohol (PVA: with an average degree of polymerization of 1799) and Casein powder (>80% DA) and Carrageenan were purchased from Marine hydro colloids Kochi, Kerala. All other chemicals used were laboratory grade. Metal used were GI sheets with 1mm thickness and plastics sheets were LDPE sheets of 1mm thickness.

LDPE based Plastic sheet and GI sheet were cut into rectangular pieces. A square portion of the pieces was marked and cleaned with sand paper. The adhesives of different compositions were applied on the square portions of the pieces and made plastics to plastics, metal to metal and metal to plastics joints. The adhesives were allowed to dry for 7 days so as the joints to adhere very well. Retention in hot water, cold water, acid (Dil HCl), base (NaOH), and heat ageing were also conducted.

RESULTS AND DISCUSSION:

Figure 1 shows the Modulus of the adhesive joints made with casein as a basis and varying PVA. The results shows that as the amount of PVA increases modulus increases and reaches a maximum and decreases on further increase in PVA content. It is evident that when PVA increases adhesive properties are improving due the increase in polarity of the compound. The OH group in PVA can enhance the bonding due to the attraction. When the amount of PVA increases beyond a specific limit, the compatibility of the two components decreases. This is reason for the decrease in adhesive strength. Therefore there is an optimum ratio of PVA casein is found to be effective in the adhesive joints. The influence is found to be similar in all types of adherents.



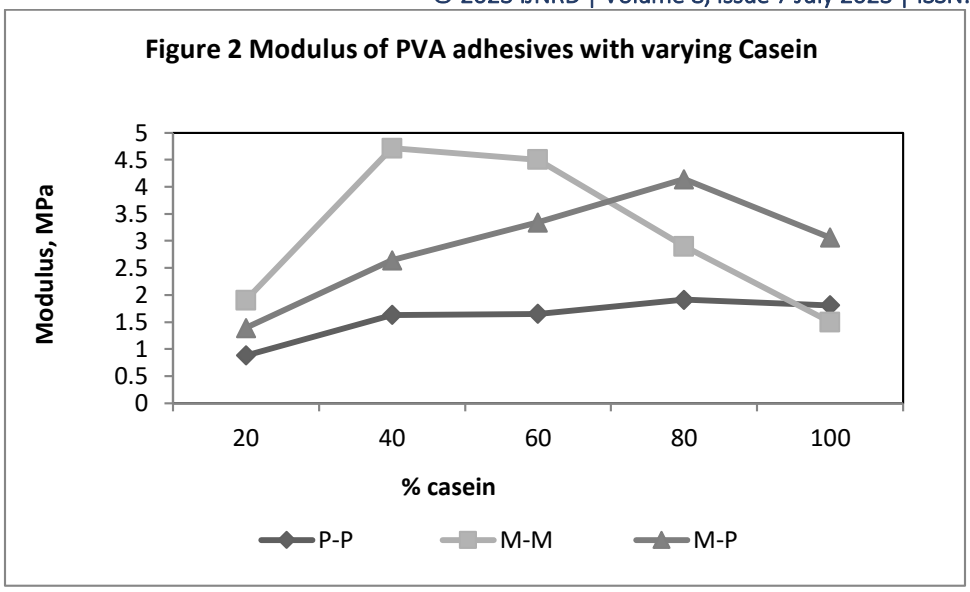


Figure 2 shows the modulus values for the adhesives with varying casein in the PVA solution. In this case metal to metal joints shows very sharp increase in modulus but plastic to plastics joints were weaker comparatively. This also shows an optimum level for the two elements as earlier. Casein contains favorable functional group to get higher joint strength with metals compared with plastics.

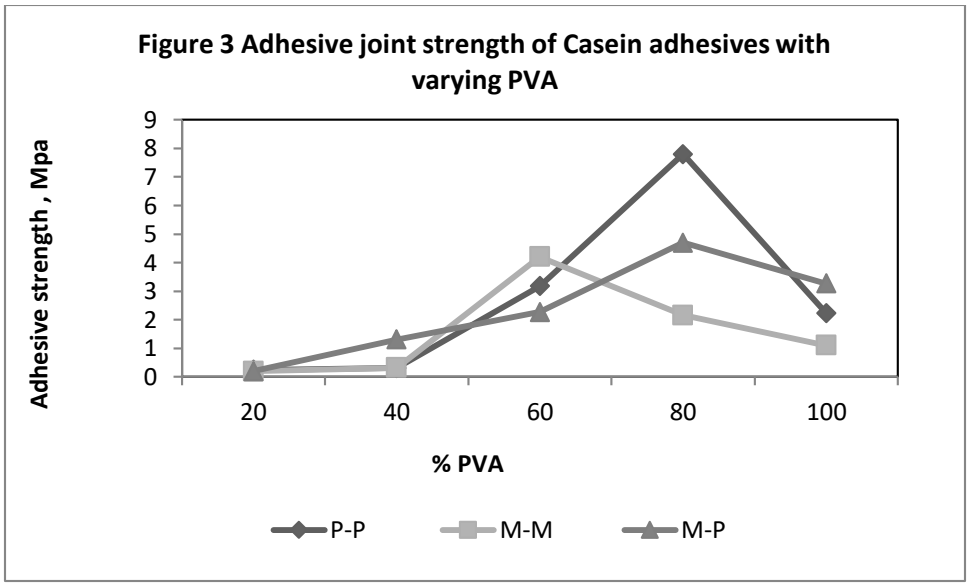


Figure 3 shows the adhesive joint strength for Casein based adhesive when PVA is added in various proportions. Figure 4 is giving the results when casein is added into PVA adhesive in various proportions. In both cases the adhesive strength increases and reaches a maximum and decreases. The adhesives are working with temporary polar attractions due to the presence of functional polar groups. The polarity increases as the second component added either Casein or the PVA up to an optimum level. This shows the optimum amount of the other component in the main matrix phase. When the second member added above the limit the phases may get immiscible and lacks the adhesive properties and the joints strength became lower [7-10].

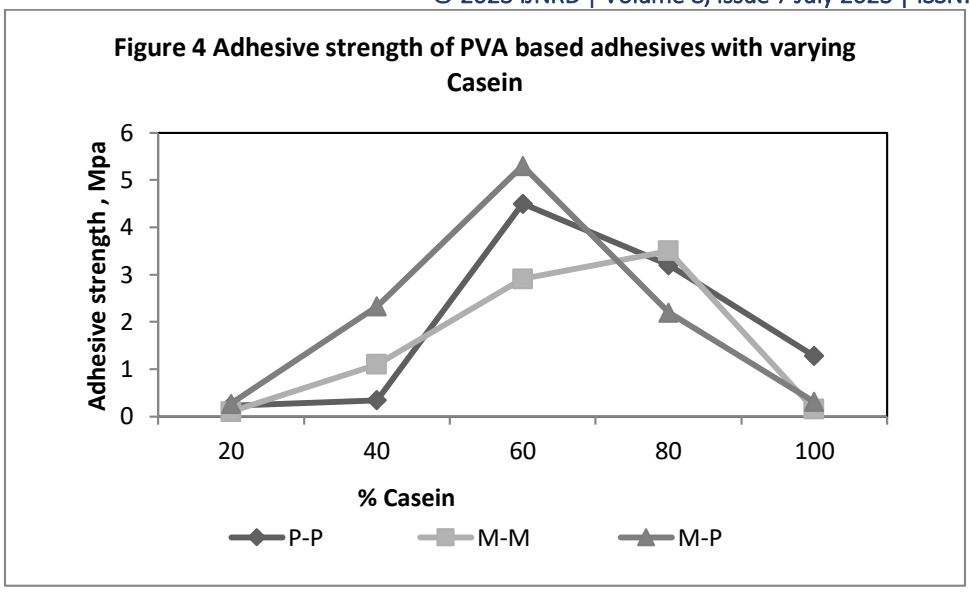
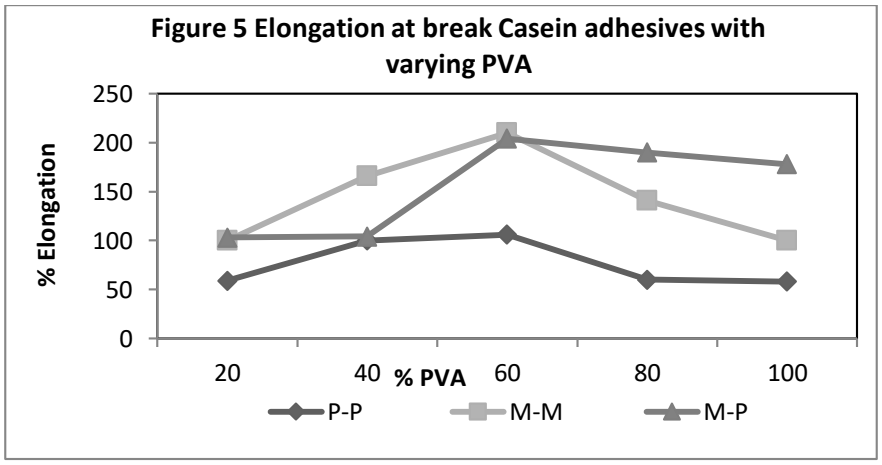
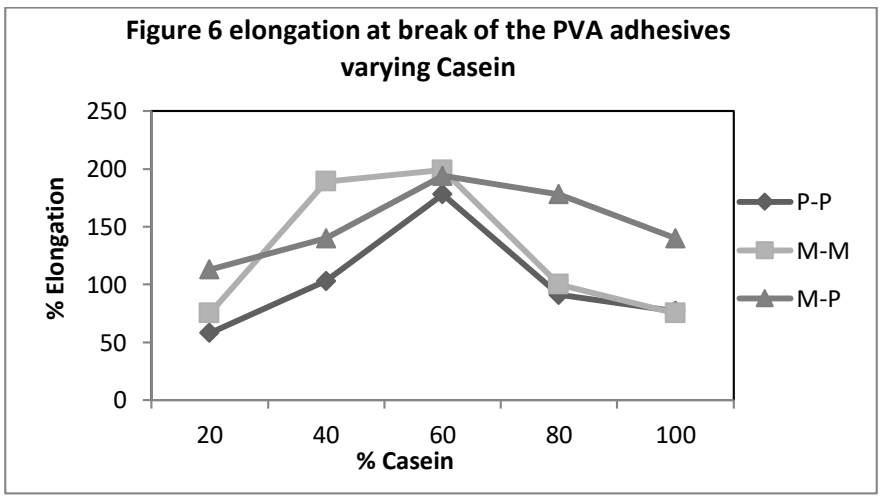


Figure 5 shows the Elongation at break for the adhesive joints; Figure 6 shows the elongation for the adhesive when Casein is added to PVA solutions. The results are as similar as adhesive properties increasing and decrease after an optimum level. When the materials are less resilient then the adhesive strength decreases. It is the region where materials lose its miscibility of phases and there the elongation properties decreases. The effect is similar in the case with PVA as the matrix phase and casein as the matrix phase.





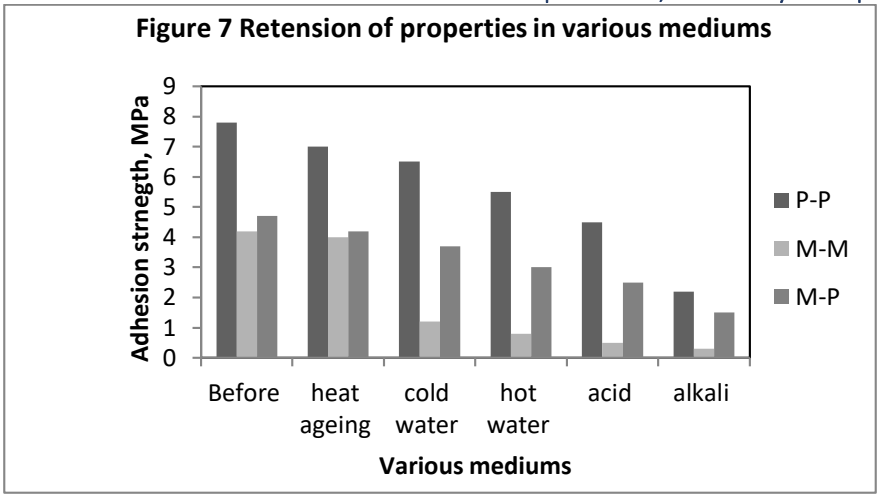


Figure 7 shows the retention in various mediums for the, Composition of Adhesive is 8% PVA in Casein like cold water, hot water, heat ageing, acid and alkali mediums. There is very minor reduction in adhesive properties after subjected to these mediums. All the joints show same pattern in the retention. It is evident from the results that plastics to plastics and plastics to metal joints are much more stable in adhesion strength compare to metal to metal joints. This is because of the lowering of a polarity of the compounds when subjected to mediums, and the free volume increases when the medium penetrated through the matrix and adhesion strength deceases.

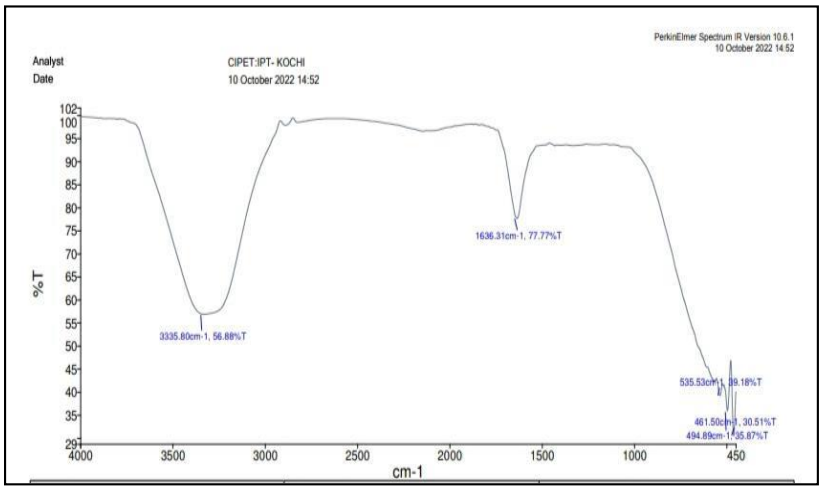


Figure 8 FTIR of PVA / Casein blend. (Composition of Adhesive is 8% PVA in Casein)

It confirms the presence of both PVA and Casein molecules. The peeks are as follows , 1461 cm^{-1} -vibration of C–H bond from CH_2 groups , 1375 cm^{-1}- methylene group and a tertiary carbon atom, 1700 and 1500 cm^{-1}- strong amide I and amide II peaks between, 3400-3000 cm^{-1}-NH group stretching at characteristic of amino acids, 3280 cm^{-1}- O–H stretching vibration of the hydroxy group, 2917 cm^{-1}- CH asymmetric stretching vibration, 1690 cm^{-1} - C=O carbonyl stretch, 1425 cm^{-1}- C–H bending vibration of CH_2 C–H deformation vibration, 1324-1081 cm^{-1} C–O stretching of acetyl groups,839 cm^{-1}C-C stretching vibration, 3335.80 cm^{-1}which is due to the hydrogen bond between OH, 3454.75 cm^{-1} - 3280 cm^{-1} - NH group and stretching vibration of NH bond and small and narrow peak at 1636.31 cm^{-1}can be seen which indicates the presence of amide peak.

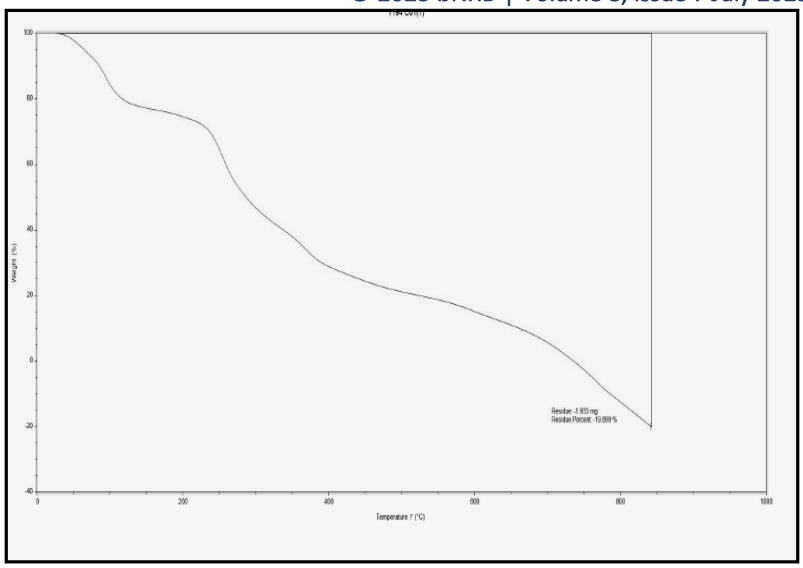


Figure 9 TGA Curve of PVA/Casein blend**,** (Composition of Adhesive is 8% PVA in Casein)

Figure 9 shows the TGA curve of PVA / casein blend (Composition of Adhesive is 8% PVA in Casein). The blends shows better retention of weight loss compare to the individual components. Therefore these blends can be used as similar to the individual components for adhesive application with better thermal resistance.

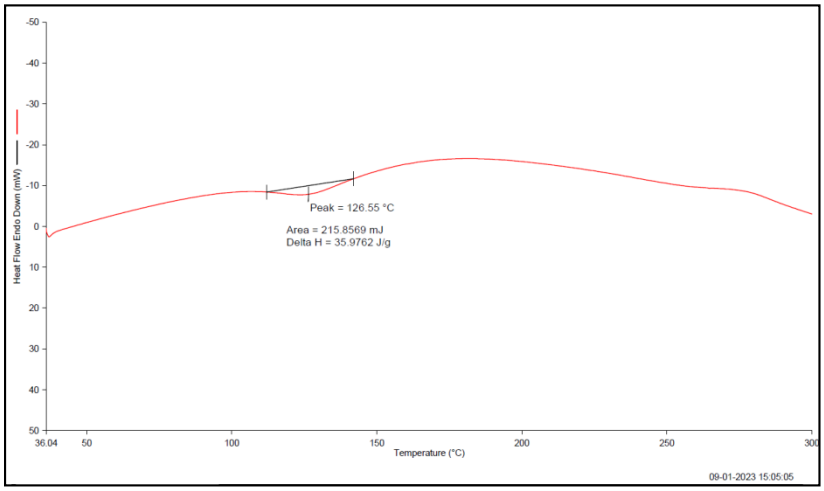


Figure 10, DSC curve of PVA / Casein blend, (Composition of Adhesive is 8% PVA in Casein)

Figure 10 shows the DSC curve for the PVA / Casein blend, (Composition of Adhesive is 8% PVA in Casein). This case also shows the thermal stability of the compound as compared with the individual polymers as matrices. The transition temperatures are as close as the individual constituents; therefore it can be used in various thermal conditions as the individual components. The melting point is around 126 ^{0}C, which will be very much useful in adhesive when its applications above room temperatures.

CONCLUSIONS :

Various proportions of PVA/ Casein blends were prepared by using PVA as matrix phase and Casein as added phase and vice versa. Al the adhesives were tried on plastics to plastics, plastics metal and metal to metal joints. It is found that these bio-based adhesives can very well replace the commercial adhesives and can reduce the environmental impact created by the non bio-based or petroleum based adhesives. The medium used were water and therefore The PVA/ Casein blends are showing good adhesive strength and resistance in hot water, cold water,

Acid and alkali and on heat ageing. FTIR, TGA and DSC characteristics are showing identical characteristics with the original materials.

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