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Effect of chemical modification on the performance of biodegradable jute yarn-Biopol® composites

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Jute yarn-Biopol® composites are prepared by hot-press moulding technique. Jute yarns of two varieties (7.36 lbs/spy and 11.86 lbs/spy) are used for composite fabrications. Effects of temperature, yarn amount, chemical modification like dewaxing (defatting), alkali treatment, graft copolymerization and orientation of yarn winding on the performance of resulting composites have been investigated. The mechanical properties like tensile strength, bending strength, impact strength and bending-E-modulus increased substantially in comparison to pure Biopol® as a result of reinforcement with jute yarns. The most remarkable observations of our present investigations include more than 150% enhancement in tensile strength, impact strength, bending-E-modulus and more than 50% enhancement in bending strength of the resulting composites as compared to pure Biopol® sheets. Amount of jute yarn, chemical modifications and measurement of mechanical properties on the direction of winding of yarns contribute significantly to the mechanical properties of resulting composites.

1. Introduction

In the modern polymer technology it is a great demand that every material should especially be adapted to the environment. Because of increasing environmental consciousness and demands of legislative authorities, the manufacture, use and removal of traditional composite structures, usually made of glass, carbon or aramid fibers embedded in epoxy, unsaturated polyester resins, polyurethane or phenolics are considered critically. By embedding natural reinforcing fibers, e.g. jute, flax, hemp, ramie, etc. into a biopolymeric matrix made of derivatives from cellulose, starch, lactic acid, etc., new fiber reinforced materials called biocomposites, were created and are still being developed [1, 2]. As far as the mechanical properties are concerned, biocomposites are comparable to the well-known glass fiber reinforced plastics. The new trends in solid waste management and rapid changes in public legislation have led scientists to increase activities on the design of materials that easily degrade under well defined environmental conditions [3, 4]. Biocomposites apart from being re-used or recycling, offer additional possibilities of a convenient removal after the end of a life time, i.e. through biodegradation or composting or combustion. As is well known [1] combustion of biocomposites maintains carbon dioxide neutrality and is completely slag-free.

The main constraint on the use of biodegradable polymers is the difference in the price of these polymers compared to bulk produced oil-based plastics [5]. Mayer and Kaplan [6] have also reviewed the cost (US$/lb) of biodegradable polymers such as starch (0.15–0.8), cellulose acetate (1.70), Biopol® (6–8), polyvinyl alcohol (1.5–2.5), polycaprolactone (2.70) and polylactic acid, PLA (1–3). According to these values, Biopol® polymers costing 6.00–8.00 US$/lb is about four to ten times more expensive than starch. According to Mar Tech report of July 1998 [7], the average cost ($/lb) of polypropylene, low-density polyethylene, and high-density polyethylene are 0.33, 0.41, and 0.37 respectively, whereas the average cost of PLA, starch based resins, and polyhydroxy alkanoates are 1.5–3.0, 1.60–2.90, and 4.00–6.30 respectively. For scientists, the real challenge lies in finding applications which would consume sufficiently large quantities of these materials to lead to price reduction, allowing biodegradable polymers to compete economically in the market.

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Poly(β-hydroxybutyrate) (PHB) (trade name: Biopol®) is a biologically produced polyester. Copolyester of 3-hydroxybutyrate(HB) and 3-hydroxyvalerate(HV) (PBHV) (trade name also Biopol®) has been isolated from *Alcaligenes eutrophus* [8]. PHBVs are highly crystalline polymers with melting points and glass transition temperatures close to polypropylene. Natural polymers are generally biodegradable but they do not possess the necessary thermal and mechanical properties for engineering plastics. On the other hand, the best engineering plastics are obtained from synthetic polymers, but they are very poor in their biodegradability characteristics. We have choosen a natural fiber (jute) and a bacterial copolyester (Biopol®) for composite fabrication with a long range objective of diversified uses of such biocomposites. Biopol has been used extensively in blending technology [9, 10], however, its use in composite fabrication is just in a very early stage [1]. Recently, the physical and mechanical properties of jute fabric- Biopol® composites have also been reported [11]. In this paper the authors have used bleached hessian cloth for composite fabrication. Gassan and Bledzki [12] have reported the influence of fiber-surface treatment on the mechanical properties of jute-polypropylene composites. In this paper we wish to report the effect of chemical treatment on the performance of jute yarn-Biopol® composites.

2. Experimental procedure

2.1. Materials

Two types of jute yarns e.g. 7.36 lbs/spy and 11.86 lbs/spy were supplied by Konark Jute Mills, Dhanamandal, Orissa, India. All the chemicals like copper sulfate, sodium periodate, sodium hydroxide, ethanol and benzene were of AnalaR grade and were used without further purification. The monomer acrylonitrile (AN) (CDH, India) was purified as reported earlier [13]. Biopol®, Poly (3-hydroxybutyrate-co-8%-3-hydroxyvalerate) was received by ICI, UK.

2.2. Chemical modifications of jute yarns

The above mentioned two types of jute yarns were washed with 2% detergent solution at 70°C for 1 h; then washed thoroughly with distilled water followed by air drying for two days and then vacuum oven drying at 70°C overnight. Three different types of surface treatment/modification of detergent washed jute yarns were used for preparation of composite materials. The defatted jute yarns were obtained by dewaxing the detergent washed oven dried samples with a 1 : 2 mixture of alcohol and benzene for 72 h at 50°C, followed by washing with distilled water. The defatted yarns were treated with 5% NaOH solution for 30 min, then washed thoroughly with distilled water, to obtain alkali treated yarns. The alkali treated yarns were subjected to graft copolymerization with AN using Cu^{2+}-IO_4^- combination as initiator in an aqueous medium. Procedure of graft copolymerization of AN was same as reported earlier [13]. By controlling the reactant concentrations, temperature and jute yarn amount the desired percentage of graft yields (GY) were obtained.

2.3. Composite fabrication

Biopol® films of 1 mm thickness were prepared by hot press technique at 180°C. Then the pre-weighted Biopol® film of required dimension was wound with jute yarns in the desired direction. The jute yarn-Biopol® composite (JYBC) was prepared by sandwiching two sheets of Biopol® films with the jute yarn wound (both sides) Biopol® film. The prepreg was prepared by heating this material at 180°C (except while studying temperature variation) for 5 minutes between two steel plates under a pressure of 0.2 MPa. This prepreg material was cooled to room temperature, then cut to the desired size in a mould and heated again for 5 minutes at 180°C under a pressure of 20 MPa to obtain the final composite material. While investigating the effect of composite fabrication temperature on the mechanical properties of JYBC, the prepreg as well as the final press were made at the respective temperature but the time and pressure were maintained the same as in composite fabrication at 180°C.

2.4. Testing

The tensile properties of the Biopol® and its composites were determined using an INSTRON (model 1026). The tensile strength (TS) measurement and three point bending test were carried out following DIN 53455 and DIN 53452 standard methods respectively. Impact strength was carried out by an Impact Tester (Zwick, Germany); using DIN 53433. All the results were taken as the average value for 5 samples.

3. Results and discussion

In order to study the reinforcement effect of different modified jute yarns with Biopol®; tensile strength (TS), bending strength (BS), impact strength (IS) and bending-E-modulus (Bm) of Biopol® sheets (2 mm thickness) prepared as above were determined and were taken as references. The enhancement of mechanical properties as a result of jute reinforcement in the Biopol® polymer has been expressed by factors e.g. tensile strength factor (Tf), bending strength factor (Bf), impact strength factor (If) and bending-E-modulus factor (Bmf). The Tf can be expressed as the ratio of tensile strength of composite (TSc) to that of pure Biopol® polymer (TS) i.e. Tf = TSc/TS. Similarly Bf = BSc/BS; If = ISc/IS and Bmf = Bmc/Bm. All the above mentioned properties of jute yarns-Biopol® composites were measured in both directions i. e. along the yarn winding direction and also perpendicular to the yarn winding direction (Fig. 1).

3.1. Effect of temperature

The effect of composite fabrication temperatures on mechanical properties of alkali treated jute yarn (11.86 lbs/spy)-Biopol® composites (jute content ca.

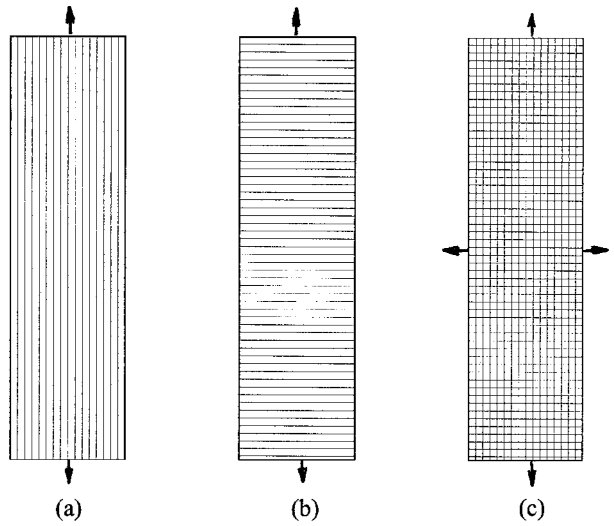

Figure 1 Schematic representation of yarn winding and mechanical properties measurement: (a) along the yarn winding direction (b) perpendicular to the yarn winding direction and (c) in either direction of cross-winding yarn based composite. [The arrow (→) depicts the direction of measurement of mechanical properties].

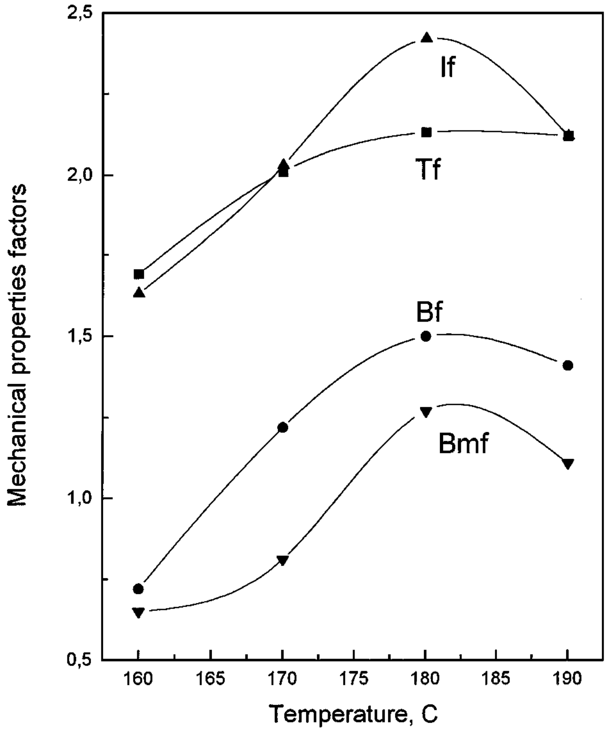

Figure 2 Effect of pressing temperature on mechanical properties of jute yarn composites along the yarn winding direction.

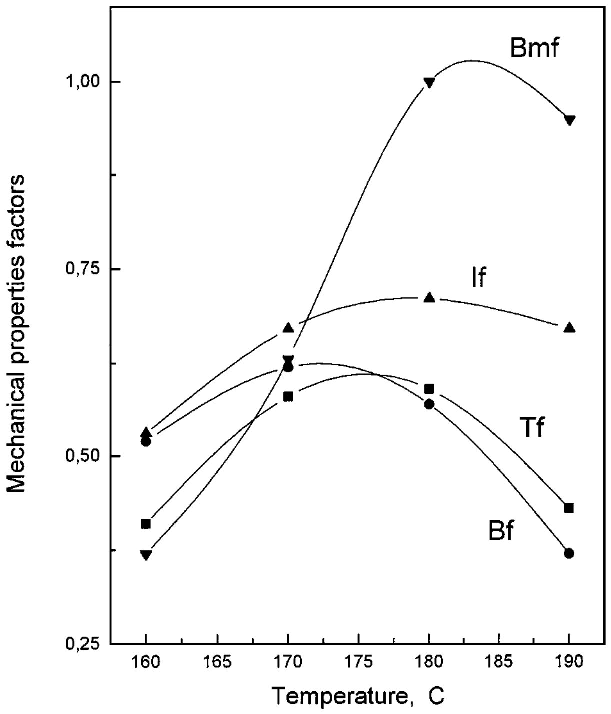

Figure 3 Effect of pressing temperature on mechanical properties of jute yarn composites perpendicular to the yarn winding direction.

15 wt%) has been investigated. The results as obtained by the measurements of the properties along the direction of yarn winding and that of perpendicular to the direction of yarn winding direction are shown in Figs 2 and 3, respectively. Most of the properties of the composites are found to increase with increasing temperature up to 180°C, and thereafter they decrease. The tensile strength factor (Tf) of composite at 180°C is 2.13 (Fig. 2) which indicates an enhancement of 113% of tensile strength in composite in comparison to pure Biopol® sheet. At 160 and 170°C the Tf values are 1.69 and 2.01 indicating 69 and 101% of enhancement in tensile strength, respectively. At 190°C there is no further change in tensile strength in comparison to the value at 180°C. From bending strength factor (Bf) values we observe 22, 52 and 41% enhancement in bending strength values of composites being fabricated at 170, 180, and 190°C, respectively. The bending strength value of the composite being fabricated at 160°C is found to be less (Bf = 0.72) than that of pure Biopol® sheet. The impact strength of the composites also show increasing trend with the increase of composite fabrication temperature from 160 to 180°C (63 to 143%). In contrast to 143% enhancement at 180°C a lower enhancement (112%) is observed at 190°C in comparison to the value at 180°C. From the Bmf values we observe that the bending-E-modulus values of composites being fabricated at 160 and 170°C are found to be less than that of the pure Biopol® sheet. However, the composites show a slight enhancement in bending-E-modulus values to 27 and 11% at composite fabrication temperature of 180 and 190°C, respectively. Here also we observe the decreasing trend in enhancement of bending-E-molulus values of the composites from 27 to 11% with an increase of the composite fabrication temperature from 180 to 190°C. With further increase of temperature to 190°C the degradation of Biopol® might have formed crotonic acid and volatile products which are responsible for the decreasing trends of mechanical properties [14]. While studying the mechanical properties of jute-Biopol® composites in the direction perpendicular to yarn winding (Fig. 3) it is observed that all mechanical properties are less than those of pure Biopol® sheets. So from the above observation it is concluded that under the present experimental conditions, jute acts as reinforcement in jute Biopol® composite along the direction of wrapping, while in perpendicular direction, jute acts only as filler thereby not enhancing the mechanical properties of the composites.

TABLE I Effect of jute amount on mechanical properties of jute-Biopol® composites

	Mechanical properties							
	Along the direction				Perpendicular to the direction			
% Jute (w/w)	Tf	Bf	If	Bmf	Tf	Bf	If	Bmf
a. Alkali treated yarn (11.86 lbs/spy)								
13.9	2.13	1.52	2.42	1.27	0.59	0.66	0.71	0.66
19.3	2.76	1.47	2.42	1.36	0.57	0.57	0.72	0.52
21.2	2.89	1.50	2.46	1.62	0.56	0.55	0.81	0.72
b. Alkali treated yarn (7.36 lbs/spy)								
10.8	2.19	1.47	2.45	1.34	0.73	0.68	1.08	0.93
15.0	2.75	1.49	2.50	1.67	0.52	0.62	1.17	0.97
22.8	2.94	1.64	2.56	1.98	0.34	0.40	1.22	1.20

3.2. Effect of jute amount

The effect of jute amount on mechanical properties of alkali treated jute yarn-Biopol® composite is presented in Table I. From the results it is observed that all mechanical properties improve with the increase of jute yarn amount. From Table I, the most remarkable observations are: (a) at 21.2% jute yarn (11.86 lbs/spy) content: tensile strength increases by 189%, bending strength by 50%, impact strength by 146% and bending-E-modulus by 162%, (b) at 22.8% jute yarn (7.36 lbs/spy) content in composite: tensile strength, bending strength, impact strength and bending-E-modulus enhance by 194, 54, 156 and 98%, respectively. The enhancement in mechanical properties is observed only when the properties are measured along the yarn winding direction. Even after increasing jute yarn amount; while measuring the properties perpendicular to the yarn wrapping direction; at 21.2% yarn (11.86 lbs/spy) content: the If (0.81) and Bmf (0.72) values approach towards the value of pure Biopol®. Again, at 22.8% yarn (7.36 lbs/spy) content: the If value (1.22) and the Bmf value (1.20) just approach to pure Biopol®. Because of enhanced, more intense interaction of thinner yarn with the matrix in comparison to thicker yarn; the former is supposed to exceed mechanical properties in the resulting composites. The more intense interaction of thinner yarn as compared to thicker yarn (the amount of both type of yarns being nearly same in both composites) is attributed to the availability of more contact surface area for the former. The increase of mechanical properties with increase of jute content, in good agreement with an earlier observation [12].

3.3. Effect of chemical treatment

In order to study the effect of different types of chemical treatment on mechanical properties of jute-Biopol® composites, jute yarn of 7.36 lbs/spy type has been investigated. The results are presented in Figs 4 and 5. Composites of alkali treated jute yarn are found to reach better mechanical properties in comparison to composites of defatted yarn as well as acrylonitrile (AN) grafted (23.5%, GY) yarn. From Fig. 4 it is observed that alkali treated yarns show an enhancement of 119, 47, 145 and 39% in contrast to an enhancement of 96, 26 105 and 49% of defatted yarns in tensile strength, bending strength, impact strength and bending-E-modulus values of the resulting composites, respectively. In defatted samples dewaxing of jute occurs which also helps to improve the fibre matrix interaction [15]. The superior mechanical properties of alkali treated jute yarn composites in comparison to defatted jute yarn composites may be attributed to improved fibre matrix interaction [16]. The alkali treatment improves the fibre surface adhesive characteristics by removing natural and artificial impurities, thereby producing a rough surface topography [17]. In other words, alkali treatment leads to fibre fibrillation, i.e. breaking down of fabrics fibre bundle into smaller fibres thereby increasing the effective surface area for contact with the matrix. It is believed that the alkali treatment results in improvement in the interfacial bonding by giving rise to additional sites of mechanical interlocking, thereby

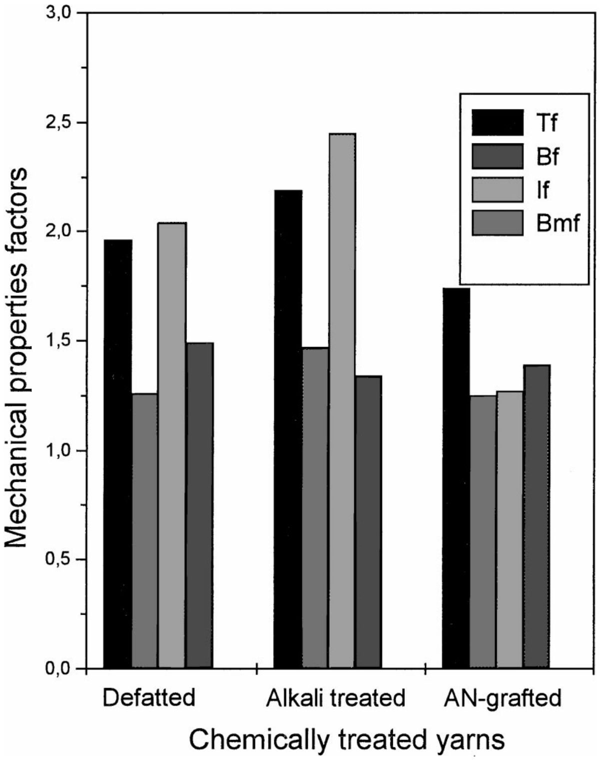

Figure 4 Mechanical properties of the composites along the yarn winding direction for differently chemically treated yarns.

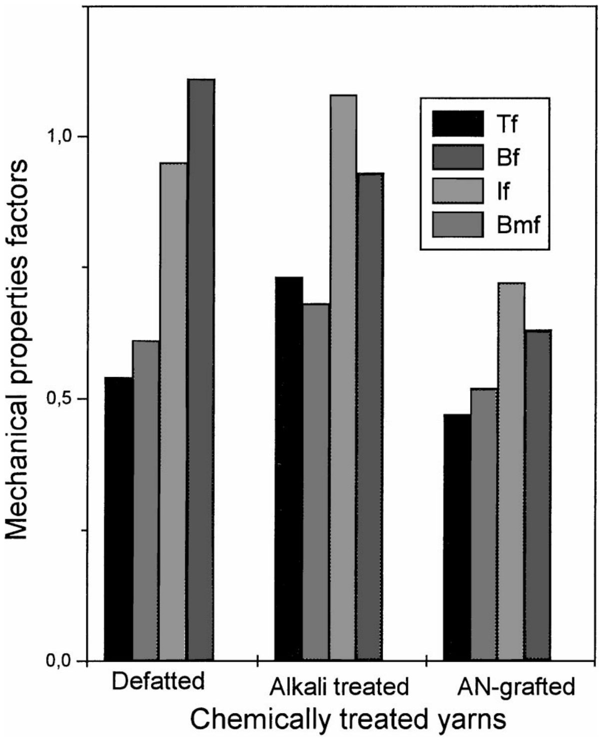

Figure 5 Mechanical properties of the composites perpendicular to the yarn winding direction for differently chemically treated yarns.

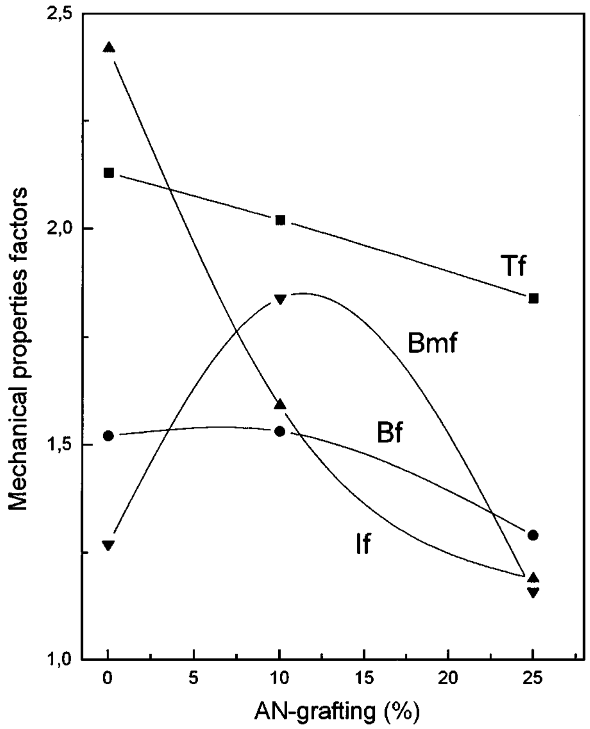

Figure 6 Effect of AN-grafting on mechanical properties of jute yarn composites along the yarn winding direction.

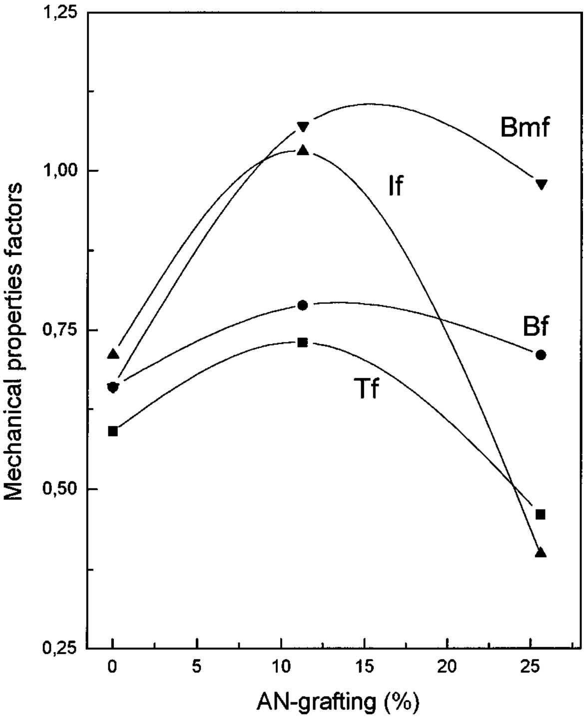

Figure 7 Effect of AN-grafting on mechanical properties of jute yarn composites perpendicular to the yarn winding direction.

promoting more resin/fibre interpenetration at the surface [18]. Although AN-grafted yarns exhibit an enhancement in mechanical properties of composites with respect to pure Biopol® sheets, the degree of enhancement is found to be less in comparison to other two types of modifications (i. e. defatted or alkali treated). From Fig. 5 we conclude that the mechanical properties of all chemically modified jute yarn composites reach less values (i.e. the values of Tf, Bf, If, and Bmf are less than 1) than the pure Biopol® sheets due to the same reason as discussed earlier.

The effect of AN-grafting onto jute yarn (11.86 lbs/spy) on the mechanical properties of resulting composites is shown in Figs 6 and 7. While studying grafting effect we have taken alkali treated yarn as the standard material for comparison. Two differently grafted yarns (10% GY and 25% GY) are taken for comparison studies. From Fig. 6 it is well observed that with the increase of percentage of GY from 10 to 25% most of the mechanical properties are found to decrease. With 10% GY yarn, the tensile strength enhanced by 102%, and with 25% GY yarn the tensile strength enhanced by 84% in comparison to pure Biopol®. However, under similar experimental conditions, an enhancement of 113% in tensile strength is observed in case of alkali treated yarn. Other mechanical properties also follow nearly the similar trend. One important observation is that 10% AN-grafted yarn-Biopol® composite gives an higher Bmf value (1.84) as compared to that of alkali treated yarn (Bmf = 1.27).

3.4. Effect of orientation of yarn winding

The effect of orientation of jute yarns on the mechanical properties of composites is represented in Fig. 8. For such studies, we have taken three types of composites: by winding the alkali treated yarns (11.86 lbs/spy) once, twice and also by cross-winding with Biopol® sheets (Fig. 1). The measurement of mechanical properties of the resulting composites from once winding and twice winding are performed along the direction and perpendicular to the direction of winding. However, for the cross-winding sample the mechanical properties measurement in both directions gave the same result. Twice

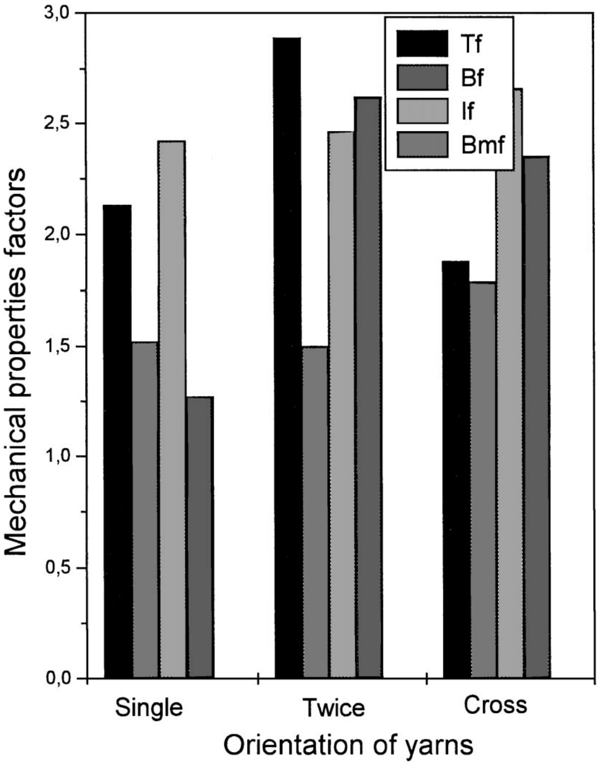

Figure 8 Effect of orientation of yarns on mechanical properties of the composites.

winding produces better mechanical properties like tensile strength, impact strength and bending-E-modulus. This enhancement in properties of composites may be due to the increased jute amount as a result of twice winding. The composite resulting from cross-winding of yarns gives a decreased value, i.e. 88% enhancement in tensile strength as compared to 133 and 189% enhancement in tensile strength values of composites resulting from once and twice winding of yarns, respectively. However, bending strength (79% enhancement) and impact strength (166% enhancement) of cross-wound composites are found to be higher when compared to those of composites resulting from once and twice winding of yarns. The decreased enhancement in tensile strength value of cross-wound composite may be attributed to the fact that only one half of the yarns which are along the direction of measurement of tensile strength attribute to the increase of tensile strength value, whereas the yarns which are perpendicularly wound in the same composite may be responsible for decrease of tensile strength value, otherwise the tensile strength value would have shown nearly the same value to that of the composite resulting from once yarn winding. Such an explanation is also based upon our experimental results so far we have mentioned while discussing the measurement of mechanical properties of the composites in the direction perpendicular to the yarn winding direction. However, the bending strength and impact strength of the cross-winding based composites show slight enhancement as compared to once and twice yarn wound composites. Such observation may be attributed to the increased jute content and/or reinforcement of jute yarns in both directions of cross-winding based composites.

4. Conclusions

Tensile strength, bending strength, impact strength and bending-E-modulus are enhanced by reinforcing Biopol® with jute yarn. Among the chemically modified yarns (defatted, alkali treated and AN-grafted); alkali treated yarns produce better mechanical properties in comparison to defatted as well as to grafted yarns. The enhancement of mechanical properties due to chemical treatment is attributed to the improved fiber matrix adhesion. The composites resulting from thinner yarns as compared to thicker ones give better mechanical properties. Temperature of composite fabrication affects the mechanical properties of the composites. Jute-Biopol® composite being fabricated at 180°C shows optimum mechanical properties. From the present investigations, the maximum enhancement of the mechanical properties in comparison to pure Biopol® so far we have achieved are 194, 79, 166 and 162% in tensile strength, bending strength, impact strength and bending-E-modulus, respectively.

Since both Biopol® and jute are biodegradable, the resulting composites are expected to be biodegradable and environmentally friendly materials. The two main reasons for the interest of biodegradable materials are: the growing problem of waste thereby resulting general shortage of landfill availability and the need for the environmentally responsible use of resources together with the the CO_2 neutrality aspect [19]. Performance limitations and high costs have restricted the adoption of biodegradable plastics to very small niches up to now. We tried to reduce the cost and enhance the properties of such biodegradable plastics by reinforcement with low cost jute. The possible applications of our jute yarn-Biopol® composites include rigid containers, consumer disposables, interior parts of automobiles, and packaging materials etc. However the future uses of such biocomposites largely depend on continued research and development since we are just at the infancy stage of these materials. The important feature of composite materials is that they can be designed and tailored to meet different requirements. Since natural fibre like jute is cheap and biodegradable, the biocomposites from jute reinfoced biodegradable polymers will render a contribution in the 21st century due to the serious environmental problem.

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