SYNTHESIS OF POLYMERIC FILM COMPOSITE AND THEIR MECHANICAL CHARECTRIZATION

FINAL SYNOPSIS

of the Thesis to be submitted for the Degree of

DOCTOR OF PHILOSOPHY

IN

POLYMER SCIENCE

To

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MAY 2012

Chapter I

INTRODUCTION

Cellulose, the most abundant natural homopolymer, is considered to be one of the most promising renewable resources and an environmentally friendly alternative to products derived from the petrochemical industry. Recently, modified cellulose has been used as reinforcements for various composites due to its excellent mechanical performance and fully biodegradable in a wide variety of environmental conditions. As a result, various cellulose-based composites have been prepared. Currently, more and more researchers are developing fully biodegradable composites, the so-called green composites, ecocomposites or biocomposites which are composed of natural fibers and natural matrices or synthetic biodegradable matrix. Composites are usually fabricated with biodegradable polymers as matrix phase and natural fibers as enhancement phase. Poly (e-caprolactone) (PCL), poly (vinyl alcohol) (PVA), poly (lactic acid) (PLA), Polypyrrolidone, poly (butylene succinate) (PBS) and poly (3-hydroxybutyrate-co-3-hydroxybutyrate) (PHBV) are most commonly used as matrix phase of composites.

Cellulose is a poly-β-1,4-D-glucopyranose and it is biodegradable, nontoxic, biocompatible, hydrophilic, safe, has high moisture-retentivity and chiral. However, cellulose has not reached its potential application in many areas because of its infusibility and insolubility. But at the same time, cellulosic fibers are hygroscopic in nature; moisture absorption can result in swelling of the fibers which may lead to micro-cracking of the composite and degradation of mechanical properties. This problem can be overcome by treating these fibers with suitable chemicals to decrease the hydroxyl groups which may be involved in the hydrogen bonding within the cellulose molecules. Chemical treatments may activate these groups or can introduce new moieties that can effectively interlock with the matrix. A number of fiber surface treatments like silane treatment, benzoylation and peroxide treatment were carried out which may result in improved mechanical performance of the fiber and composite. By limiting the substitution reaction on the surface of the fibers, good mechanical properties were obtained and a degree of biodegradability was maintained. As a result, various cellulose based composites have been prepared. However, there is no literature regarding the composite films of modified cellulose/PLA; modified cellulose/PVA; modified cellulose/PVA/ poly (lactic acid); modified cellulose/PVA/polypyrrolidone; modified cellulose/ polypyrrolidone. Up to know, there is no information on mechanical properties, moisture absorption, gas barrier and environmental biodegradability of the above mentioned film composites. The purpose of this work is to produce biodegradable film composites, which can be useful for membrane and packaging applications. In this investigation, mechanical properties, gas barrier properties, water absorption behavior, biodegradable studies and the morphology of the ensuing composites were evaluated.

Chapter II

PREPARATION AND PROPERTIES OF COMPOSITE FILMS FROM MODIFIED CELLULOSE FIBRE-REINFORCED WITH PLA

Now a day there is an emerging interest in replacing non-renewable additives with biodegradable compounds. Cellulose plays very important role in this modification. Their low cost and low density associated with high specific mechanical properties represent a good renewable and biodegradable alternative to the most commonly used synthetic reinforcement. The cellulose was modified by using 2-(Trifluromethyl) benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by solubility and IR studies. The biodegradable composite films were developed by film casting method using modified cellulose with Poly (lactic acid) in different compositions. The film composite were characterized by mechanical, moisture absorption, water vapor permeability, oxygen permeability and biodegradable properties.

Modification of cellulose

Cellulose was treated with sodium hydroxide solution at room temperature and stirred for 2hrs. Then solid obtained was filtered off. Salt formation was confirmed by solubility test, since it is freely soluble in water. This salt was treated with 2-(Trifluromethyl) benzoylchloride in presence of pyridine as a base cum solvent and stirred overnight at 100^oC. Then dumped in to water; solid was filtered off. This product was confirmed by I.R analysis, which shows the absence of peak at 3332 cm^{-1}.

Preparation of films

Modified cellulose was taken in a water with Poly (lactic acid) in different composition like 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05 ratio. The reaction mixture was heated to 100^oC for 24 hrs. After 24 hrs the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed before by mould releasing spray and dried under vacuum oven at 100^oC to remove water contents completely. After complete drying, the films are stored in moisture free environment.

Moisture absorption experiments

From the composite sheets, all the specimens for moisture absorption experiments were cut with dimensions of 30 mm by 10 mm. Moisture absorption measurements were performed at 25^oC. Specimens were thoroughly washed and then vacuum dried until a constant weight was attained prior to the absorption experiments. At predetermined intervals, specimens were taken out from the chambers and weighed using a PGB200 model analytical balance.

The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity, intimately relates to such composite properties as mechanical strength, dimensional stability and appearance. Though the poly (lactic acid) has been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties. Moisture absorption test was carried for all the ten composite films in which the modified cellulose and matrix poly lactic acid are in the ratio of 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05. It was observed that as the percentage of modified cellulose increases, moisture absorption decreases. This behavior clearly reflects the presence of hydrophobic moieties onto the fiber surface increase in their resistance towards moisture.

Soil burial degradation experiments

Under moisture controlled conditions soil burial degradation experiments were carried out at ambient temperature. Specimens of each composite were placed in a series of boxes containing moisturized soil. The specimens (30 X 10 mm) were buried 100 mm beneath the surface of soil which was regularly moistened with distilled water. At predetermined time points the samples were removed, carefully washed with distilled water in order to ensure the stop of the degradation, dried at room temperature to a constant weight and then were stored in darkness. The specimens were weighed on the PGB200 model analytical balance in order to determine the average weight loss.

Biodegradation of materials occurs in various steps. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to metabolization of the fragments. Either way, eventually the chain fragments become short enough to be converted by microorganisms.

The studies on biodegradation behavior are important for the application of biocomposites in environment. In this work, soil burial experiments were performed for all the ten ratio films. Note that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films weight decrease for 2 days is average 3% and it decreases gradually as the time increase and after 18 days average weight decrease is 16%. The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

Mechanical testing

Tensile strength, Young's Modulus and Elongation at break were measured according to the ASTM standard method D882-Test method A (ASTM 1997) with application of an Lloyd universal tensile machine with a 5 KN capacity at 23±2^{o}C and 48±5% RH. Test specimens with a length of 30 mm and a width of 10 mm were cut from composite sheets. All specimens were equilibrated in a chamber kept at 18°C and 35% relative humidity for 24 hr before testing. All these tests were conducted at ambient temperature and an average value of four repeated tests was taken for each material.

It was observed that tensile strength and Young's modulus of films increases as the percentage composition of the modified cellulose increases. This enhancement indicates the effectiveness of the modified cellulose as reinforcement. However, a decrease in elongation at break is observed as the percentage composition of modified cellulose increases. With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young's modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material.

Oxygen permeability test

In accordance with ASTM D3985 (ASTM 1995), the oxygen transmission rate (OTR) was determined. The film samples were equilibrated at 22 ± 2°C and 48 ± 5% RH for at least 48 hr in a controlled environment cabinet containing a saturated magnesium nitrate solution prior to the analysis. Oxygen permeability (OP) was calculated by the multiplication of the OTR at steady state by the average film thickness divided by the partial pressure difference between the two sides of the film.

Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in high elastic state. The gas permeability of crystalline polymer is much lower. The high molecular weight glassy polymers with rigid chains have very low gas permeability. With decreasing chain flexibility gas permeability decreases. Closer packing of the molecules supports permeability resistance.

Generally, hydrophilic polymeric films have shown good oxygen barrier property. There was an improvement in oxygen barrier properties of the films as the percentage of modified cellulose increases. It was observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fibre and matrix decreases. This resulted in a phase separation among the main components where the film could not be formed well, facilitating the oxygen permeation. So, it was more advantageous to improving the gas barrier properties by increasing the percentage of modified cellulose. This result indicates the potential of these films to be used as a natural packaging to protect food from oxidation reactions.

Water vapour permeability test

Based on the ASTM E96-9223 the gravimetric modified cup water method was used to determine water vapor permeability (WVP). Film samples were tested in circular test cups made of polymethylmethacrylate (PMMA). The fan speeds in the cabinets were set at an air velocity of 185 m min^{-1}. The weight loss was monitored until it was certain that water vapor transmission through the film samples had attained a steady state.

The water vapour permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. It was observed that there is a small decrease in water vapor trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. The comparison between OTR and WVTR indicates that modified cellulose is greatly effective in obstructing the oxygen permeation, but less effective in retarding the water vapor permeation. This results shows that these films may impede moisture transfer between the surrounding atmosphere and food, or between two components of a heterogeneous food product. This property is very much use full in packaging application.

Scanning electron microscopy

For the evaluation of the film microstructure scanning electron microscopy (SEM) was used. Before the analysis the samples were sputter-coated with a thin layer of gold to avoid electrical charging. It can be argued that there is an improvement of interfacial strength in the film composite as the percentage composition of modified cellulose increases. In other words bulk fibre reinforcing film composites have the most uniform distribution of fibre and the most compatible interface in film composite.

Conclusions

Composites were developed by film casting method. Moisture absorption results shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less. Film composites produced by this method shows very good biodegradation behavior, which renders them advantageous in terms of environmental protection. The produced film composites possess higher tensile strength as the proportion of modified cellulose increases and higher elongation at break as the proportion of PLA increases. So modified cellulose plays vital role in increasing the tensile strength of film composites.OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. Hence these films can be used as a packaging to protect food from oxidation reaction and moisture.

Chapter III

PREPARATION AND PROPERTIES OF BIODEGRADABLE FILM COMPOSITES USING MODIFIED CELLULOSE FIBRE-REINFORCED WITH PVA

Cellulose has a potential to become a key resource in the development of biodegradable film composites. In this work cellulose was modified by using 2-(Trifluromethyl)benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by IR studies. The biodegradable composite films were developed by film casting method using modified cellulose with Poly (vinyl alcohol) in different compositions. The film composites were characterized by mechanical, moisture absorption, gas barrier and biodegradable properties. Obtained films were shown transparency, flexibility and displayed good mechanical properties. Film composites also showed good biodegradability. Better barrier properties showed by film composites as the percentage of modified cellulose increased. This indicates the importance of modified cellulose as a reinforcing agent. After evaluating these properties of film composites we came to conclusion that, these biocomposites can use to membrane and packaging applications.

Preparation of films

Modified cellulose of 2–Trifluromethyl benzoylchloride was taken in a water and acetonitrile with Poly(vinyl alcohol) in different composition like 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05 ratio. The reaction mixture was heated to 100^{o}C for 24hrs. After 24hrs the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed before by mould releasing spray and dried under vacuum oven at 100^{o}C to remove water contents completely. After complete drying, the films are stored in moisture free environment.

Soil burial degradation experiments

In this work, soil burial experiment were performed for all the ten 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05 ratio films. The studies on biodegradation behavior are important for the application of biocomposites in environment. We observed that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films weight decrease for 2 days is average 3% and it decreases gradually as the time increase and after 18 days average weight decrease is 17%. Crystalline regions are more difficult to degrade. The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameter. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

Moisture absorption behavior

Moisture absorption test was carried for all the ten composite films in which the modified cellulose and matrix polyvinyl alcohol are in the ratio of 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10, and 95:05. We observed that as the percentage of modified cellulose increases, moisture absorption decreases. The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity, intimately relates to such composite properties as mechanical strength, dimensional stability and appearance. Though the polyvinyl alcohol has been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties. This behavior clearly reflects the presence of hydrophobic moieties onto the fiber surface increase in their resistance towards moisture.

Mechanical properties

Tensile properties of all the ten 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10 and 95:05 ratio films are evaluated. We observed that tensile strength and Young's modulus of films increases as the percentage composition of the modified cellulose increases. This enhancement indicates the effectiveness of the modified cellulose as reinforcement. However, a decrease in elongation at break is observed as the percentage composition of modified cellulose increases. With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young's modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material.

Oxygen Permeability Test

Generally, hydrophilic polymeric films have shown good oxygen barrier property. We observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. There was an improvement in oxygen barrier properties of the films as the percentage of modified cellulose increases. It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fibre and matrix decreases. This resulted in a phase separation among the main components where the film could not be formed well, facilitating the oxygen permeation. So, it was more advantageous to improving the gas barrier properties by increasing the percentage of modified cellulose. This result indicates the potential of these films to be used as a natural packaging to protect food from oxidation reactions.

Water vapour permeability test

The water vapour permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. It was observed that there is a small decrease in water vapor trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. The comparison between OTR and WVTR indicates that modified cellulose is greatly effective in obstructing the oxygen permeation, but less effective in retarding the water vapor permeation. This results shows that these films may impede moisture transfer between the surrounding atmosphere and food or between two components of a heterogeneous food product. This property is very much use full in packaging application.

Conclusions

We have successfully prepared biodegradable film composites using modified cellulose fibre-reinforced with poly(vinyl alcohol). Film composites produced by this method shows very good biodegradation behavior. This renders them advantageous in terms of environmental protection. Moisture absorption results shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less. The produced film composites possess higher tensile strength as the proportion of modified cellulose increases and higher elongation at break as the proportion of PVA increases. So modified cellulose plays vital role in increasing the tensile strength of film composites. OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. Hence these films can be used as a packaging to protect food from oxidation reaction and moisture.

Chapter IV

PREPARATION AND INVESTIGATION OF GAS BARRIER, MECHANICAL AND BIODEGRADABLE PROPERTIES OF HYBRID FILM COMPOSITES OF MODIFIED CELLULOSE - PVA/ PLA

During the last decades, cellulose fibers have been investigated as reinforcement in polymer composites for an increasing number of applications. Their low cost and low density associated with high specific mechanical properties represent a good renewable and biodegradable alternative to the most commonly used synthetic reinforcement. The cellulose was modified by using 2-(Trifluromethyl) benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by IR studies. The hybrid biodegradable composite films were developed by film casting method using modified cellulose with Poly (vinyl alcohol) and Poly (lactic acid) in different compositions. The film composites were characterized by mechanical, moisture absorption, gas barrier and biodegradable properties. The films obtained were shown to be flexible, displayed better mechanical properties. The main conclusion from this work is that modified cellulose fibers can also be used to enhance the barrier properties of biocomposites of intrest, for instance, packaging and membrane applications.

Preparation of films

Modified cellulose of 2-(Trifluromethyl)benzoylchloride was taken in a water with Poly (vinyl alcohol) and Poly (lactic acid) in different composition like 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40, and 55:05:40 ratio. The reaction mixture was heated to 100^0c for 24hr. After 24hr, the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed before by mould releasing spray and dried under vacuum woven at 100^{o}C to remove water contents completely. After complete drying, thin transparent film was obtained.

Oxygen Permeability Test

Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in high elastic state. The gas permeability of crystalline polymer is much lower. The high molecular weight glassy polymers with rigid chains have very low gas permeability. With decreasing chain flexibility gas permeability decreases. Closer packing of the molecules supports permeability resistance.

Oxygen permeation rates for all the ten films in which the modified cellulose, poly (vinyl alcohol)l and poly (lactic acid) are in the ratio of 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40, and 55:05:40 were evaluated. We observed that there was an improvement in oxygen barrier properties of the films as the percentage of modified cellulose increases. It was observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fibre and matrices decreases. This resulted in a phase separation among the main components where the film could not be formed well, facilitating the oxygen permeation. So, it was more advantageous to improving the gas barrier properties by increasing the percentage of modified cellulose. This result indicates the potential of these films to be used as a natural packaging to protect food from oxidation reactions.

Water Vapour Permeability Test

The water vapour permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. It was observed that there is a small decrease in water vapour trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. The comparison between OTR and WVTR indicates that modified cellulose is greatly effective in obstructing the oxygen permeation, but less effective in retarding the water vapor permeation. This results shows that these films may impede moisture transfer between the surrounding atmosphere and food, or between two components of a heterogeneous food product. This property is very much use full in packaging application.

Moisture absorption behavior

The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity, intimately relates to such composite properties as mechanical strength, dimensional stability and appearance. Though the poly (lactic acid) has been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties. Moisture absorption test was carried for all the ten composite films. We observed that as the percentage of modified cellulose increases, moisture absorption decreases. This behavior clearly reflects the presence of hydrophobic moieties onto the fiber surface increase in their resistance towards moisture.

Biodegradation in soil

The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. The studies on biodegradation behavior are important for the application of biocomposites in environment. In this work, soil burial experiments were performed for all the ten films. Note that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films weight decrease for 2 days is average 3% and it decreases gradually as the time increase and after 18 days average weight decrease is 17%. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

Mechanical properties

It was observed that tensile strength and Young's modulus of films increases as the percentage composition of the modified cellulose increases. This enhancement indicates the effectiveness of the modified cellulose. However, a decrease in elongation at break is observed as the percentage composition of modified cellulose increases. With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young's modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material.

Conclusions

OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. Moisture absorption results shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less. The produced film composites possess higher tensile strength as the proportion of modified cellulose increases and higher elongation at break as the proportion of PVA increases. So modified cellulose plays vital role in increasing the tensile strength of film composites. Film composites produced by this method shows very good biodegradation behavior, which renders them advantageous in terms of environmental protection. The incorporation of cellulose fiber reinforced mechanically the films, with increasing the tensile strength, reducing the oxygen and water vapor permeabilities. Apart from that the films produced are transparent and this transparency indicates the good dispersion of fiber in to the matrices. These prominent properties could be exploited

Chapter V

PREPARATION AND CHARACTERIZATION OF MODIFIED CELLULOSE FIBER-REINFORCED POLY(VINYL ALCOHOL)/POLYPYRROLIDONE HYBRID FILM COMPOSITES

In this work cellulose was modified by using 2-(Triflurommethyl) benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by IR studies. The biodegradable composite films were developed by film casting method using modified cellulose with Poly (vinyl alcohol) and Polypyrrolidone in different compositions. Film composites showed good biodegradability. Better barrier and mechanical properties showed by film composites as the percentage of modified cellulose increased. This indicates the importance of modified cellulose as a reinforcing agent. After analyzing these properties of film composites we came to conclusion that, these biocomposites can use to membrane and packaging applications.

Preparation of films

Modified cellulose of 2–Triflurommethyl benzoylchloride was taken in a water with Polyvinyl alcohol and Polypyrrolidone (in absolute alcohol) in different composition like 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40 and 55:05:40 ratio respectively. The reaction mixture was heated to 100^{o}C for 24hrs. After 24hrs the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed before by mould releasing spray and dried under vacuum oven at 100^{o}C to remove water contents completely. After complete drying, the films are stored in moisture free environment.

Comparative Studies on the Mechanical properties of the composites

The prime consideration in determining the general utility of a polymer is its mechanical behavior, that is, its deformation and flow characteristics under stress. The mechanical behavior of a polymer can be characterized by its stress-strain properties. This often involves observing the behavior of a polymer as one applies stress to it in order to elongate it to the point where it ruptures.

Mechanical properties of all the ten 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40 and 55:05:40 ratio films were evaluated. We observed that tensile strength and Young’s modulus of films increases as the percentage composition of the modified cellulose increases. This enhancement indicates the effectiveness of the modified cellulose as reinforcement. However, a decrease in elongation at break is observed as the percentage composition of modified cellulose increases.

With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young’s modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material. From this investigation, it is clear that modified cellulose composites gained huge mechanical properties over the matrices and thus indicated good fiber-matrix adhesion.

Biodegradation in soil for film composites

The studies on biodegradation behavior are important for the application of biocomposites in environment. In this work, soil burial experiments were performed for all the ten film composites. For all the films weight decrease for 2 days is average 4% and it decreases gradually as the time increase and after 18 days average weight decrease is 21%.

Cellulose molecules have two regions: one of which, called ‘crystalline cellulose’ is composed of highly-oriented molecules and other one called ‘amorphous cellulose’, comprises less-oriented molecules. The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

Oxygen Permeability Test

Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in high elastic state. The gas permeability of crystalline polymer is much lower. The high molecular weight glassy polymers with rigid chains have very low gas permeability. With decreasing chain flexibility gas permeability decreases. Closer packing of the molecules supports permeability resistance. We observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage of modified cellulose increases, crystallinity of the film composite increases and as the percentage of polyvinyl alcohol decreases, flexibility of the film composite decreases. It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. Generally, hydrophilic polymeric films have shown good oxygen barrier property. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fiber and matrix decreases. This resulted in a phase separation among the main components where the film could not be formed well.

Water vapour permeability test

Resistance to water vapour permeability is an important requirement in various applications like packaging, building constructions etc. We observed that there is a small decrease in water vapor trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. The comparison between OTR and WVTR indicates that modified cellulose is greatly effective in obstructing the oxygen permeation, but less effective in retarding the water vapor permeation.

The water vapor permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. This results shows that these films may impede moisture transfer between the surrounding atmosphere and food or between two components of a heterogeneous food product. This property is very much use full in packaging application.

Moisture absorption behavior

Moisture absorption test was carried for all the ten composite films. The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity**,** which relates to composite properties like mechanical strength, dimensional stability and appearance. Table 5 shows the moisture absorption behavior for all the ten films. It observed that as the percentage of modified cellulose increases, moisture absorption decreases.

Though the Polyvinyl alcohol and Polypyrrolidone have been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties. This behavior clearly reflects the presence of hydrophobic moieties onto the fiber surface increase in their resistance towards moisture.

Conclusions

Modification of cellulose by using 2-trifluoromethyl benzoylchloride has been found to be key investigation in this work. I have successfully prepared biodegradable film composites using modified cellulose fiber-reinforced with Poly (vinyl alcohol)/Polypyrrolidone. The produced film composites possess higher tensile strength and Young's Modulus as the proportion of modified cellulose increases. So modified cellulose plays vital role in increasing the mechanical strength of film composites. Film composites produced by this method shows very good biodegradation behavior. This renders them advantageous in terms of environmental protection. OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. Hence these films can be used as a packaging to protect food from oxidation reaction and moisture. Moisture absorption results shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less.

Chapter VI

PREPARATION AND CHARACTERIZATION OF MODIFIED CELLULOSE FIBER-REINFORCED POLYPYRROLIDONE FILM COMPOSITES

Cellulose was modified by using 2-(Trifluromethyl) benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by IR studies. The biodegradable composite films were developed by film casting method using modified cellulose with Polypyrrolidone in different compositions. Better barrier and mechanical properties showed by film composites as the percentage of modified cellulose increased. Film composites showed good biodegradability. This indicates the importance of modified cellulose as a reinforcing agent. After evaluating these properties of film composites we came to the conclusion that, these biocomposites can use to membrane and packaging applications.

Preparation of films

Modified cellulose of 2–Trifluromethyl benzoylchloride was taken in a water with Polypyrrolidone (in absolute alcohol) in different composition like 10:90, 30:70, 50:50, 70:30 and 90:10 ratio respectively. The reaction mixture was heated to 100^{o}C for 24hrs. After 24hrs the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed before by mould releasing spray and dried under vacuum oven at 100^{o}C to remove water contents completely. After complete drying, the films are stored in moisture free environment.

Oxygen Permeability Test

It was observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage of modified cellulose increases, crystallinity of the film composite increases and as the percentage of Polypyrrolidone decreases, flexibility of the film composite decreases. Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in high elastic state. The gas permeability of crystalline polymer is much lower. With decreasing chain flexibility gas permeability decreases. Closer packing of the molecules supports permeability resistance.

It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. Generally, hydrophilic polymeric films have shown good oxygen barrier property. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fiber and matrix decreases. This resulted in a phase separation among the main components where the film could not be formed well.

Water vapour permeability test

The water vapor permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. It was observed that there is a small decrease in water vapor trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. This results shows that these films may impede moisture transfer between the surrounding atmosphere and food or between two components of a heterogeneous food product. This property is very much use full in packaging application.

Mechanical properties

The mechanical behavior of a polymer can be characterized by its stress-strain properties. This often involves observing the behavior of a polymer as one applies stress to it in order to elongate it to the point where it ruptures. Five types of composites were prepared based on modified cellulose reinforced with Polypyrrolidone matrix. We observed that tensile strength and Young's modulus of films increases as the percentage composition of the modified cellulose increases. This enhancement indicates the effectiveness of the modified cellulose as reinforcement.

With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young's modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material.

Moisture absorption behavior

The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity**,** which relates to composite properties like mechanical strength, dimensional stability and appearance. Moisture absorption test was carried for all the five composite films.

It was observed that as the percentage of modified cellulose increases, moisture absorption decreases.

Though the Polypyrrolidone have been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties.

Biodegradation in soil for film composites

In the present work, we observed that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films weight decrease for 2 days is average 3% and it decreases gradually as the time increase and after 18 days average weight decrease is 17%. The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. All the ten film composites showed almost same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact.

Conclusions

I have successfully prepared biodegradable film composites using modified cellulose fiber-reinforced with Polypyrrolidone. Modification of cellulose by using 2-(Triflurومethyl) benzoylchloride has been found to be key investigation in this work. OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. Hence these films can be used as a packaging to protect food from oxidation reaction and moisture. The produced film composites possess higher tensile strength and Young's Modulus as the proportion of modified cellulose increases. So modified cellulose plays vital role in increasing the mechanical strength of film composites. Moisture absorption results shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less. Film composites produced by this method shows very good biodegradation behavior. This renders them advantageous in terms of environmental protection.

Chapter VII

BIOCOMPOSITES PREPARATION AND CHARACTERIZATION BY 2-FLUOROBENZOYL CHLORIDE MODIFIED CELLULOSE FIBRE WITH PVA / PLA

The cellulose was modified by using 2-fluoro benzoylchloride by base catalyzed reaction. Modification of cellulose was confirmed by IR studies. The hybrid biodegradable composite films were developed by film casting method using modified cellulose with Poly (vinyl alcohol) and Poly (lactic acid) in different compositions. Obtained films showed better biodegradability. Better barrier properties and higher mechanical properties showed by film composites as the percentage of modified cellulose increased. This indicates the importance of modified cellulose as a reinforcing agent. After analyzing these properties of film composites we came to conclusion that these biocomposites can use to membranes and packaging applications.

Modification of cellulose

Cellulose was treated with sodium hydroxide solution at room temperature and stirred for 2 hrs. Then solid obtained was filtered off. Salt formation was confirmed by solubility test, since it is freely soluble in water. This salt was treated with 2-flouro benzoyl chloride in presence of pyridine as a base cum solvent and stirred overnight at 100^{o}C. Then dumped in to water solid was filtered off. This product was confirmed by I.R analysis, which shows the absence of peak at 3332 cm^{-1}.

Preparation of films

Modified cellulose of 2–fluro benzoyl chloride was taken in a water with Poly (vinyl alcohol) and Poly(lactic acid) in different composition like 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40, and 55:05:40 ratio, The reaction mixture was heated to 100^{0}C for 24hr. After 24hr, the reaction mass was turned to viscous state, it was allowed to room temperature and spread on the Teflon mould which was sprayed before by mould releasing spray and dried under vacuum woven at 100^{o}C to remove water contents completely. After complete drying, thin transparent film was obtained.

Biodegradation in soil

The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) define degradable plastics as those which undergo a significant change in chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties, as measured by standard methods. Biodegradable plastics undergo degradation from the action of naturally occurring microorganisms such as bacteria, fungi and algae. The studies on biodegradation behavior are important for the application of biocomposites in environment.

Materials must meet specific criteria set out by the ASTM and ISO in order to be classified as biodegradable. In general, the likelihood of microbial attack on a material is dependent on the structure of the polymer. When examining polymer materials from a scientific standpoint, there are certain ingredients that must be present in order for biodegradation to occur. Most importantly, the active microorganisms must be present in the disposal site. The organism type determines the appropriate degradation temperature, which usually falls between 20 to 60^{o}C. The disposal site must be in the presence of oxygen, moisture, and mineral nutrients, while the site pH must be neutral or slightly acidic.

Biodegradation of materials occurs in various steps. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to metabolization of the fragments. Either way, eventually the chain fragments become short enough to be converted by microorganisms.

The design of a composite should be a polymer matrix (plastic material) forms a dominant phase around a filler material. The filler is present in order to increase mechanical properties, and decrease material costs. Poly (lactic acid) is the common biopolymer which is produced by microbial fermentation. It is produced by the condensation of lactic acid, which is obtained through fermentation processes. Research has shown that poly (vinyl alcohol) is an appropriate polymer to use as a matrix in natural fiber- reinforced composites, as it is highly polar and biodegradable. So combination of Poly (lactic acid) and Poly (vinyl alcohol) is a value added process.

The ability of films to degrade depends greatly with physico-chemical characteristics of the substrate, such as the degree of crystallinity and polymerization of cellulose, of which the crystallinity degree of cellulose is the most important structural parameters. Crystalline regions are more difficult to degrade. Modification of cellulose decreases the crystallinity of the cellulose fiber.

However, in this work, we used modified cellulose as a filler and combination of PVA and PLA as a matrix. Soil burial experiments were performed for all the ten 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40 and 55:05:40 ratio films. We observed that weight loss shows an approximately linear relation with degradation time for all the ten films. For all the films, weight decrease for 2 days is average 3% and it decreases gradually as the time increase and after 18 days, average weight decrease is 18%. All the ten film composites showed almost the same resistance to microorganism attack in the soil. As the microorganism attacks, the composites lose their structural integrity. Undoubtedly, the results obtained herein reveal that the film composites will not cause any deleterious ecological impact. In other words, the film composites are fully biodegradable.

Moisture absorption behaviour

The moisture absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity which relates to composite properties as mechanical strength, dimensional stability and appearance. Though the poly (lactic acid) and poly (vinyl alcohol) have been considered as one of the most promising materials for biodegradable plastics, but because of its poor resistance to water absorption, limits its wide applications. Addition of fillers is an effective way of decreasing its sensitivity to moisture and improving mechanical properties.

Moisture absorption test was carried for all the ten composite films in which the modified cellulose , poly (vinyl alcohol) and poly (lactic acid) are in the ratio of 10:50:40, 15:45:40, 20:40:40, 25:35:40, 30:30:40, 35:25:40, 40:20:40, 45:15:40, 50:10:40, and 55:05:40. We observed that as the percentage of modified cellulose increases, moisture absorption decreases.

Oxygen Permeability Test

Oxygen permeability depends on chain flexibility, phase and physical state of the polymer and packing of its molecules. The most permeable polymers are amorphous, with very flexible chains, in high elastic state. The gas permeability of crystalline polymer is much lower. The high molecular weight glassy polymers with rigid chains have very low gas permeability. With decreasing chain flexibility gas permeability decreases. Closer packing of the molecules supports permeability resistance.

It was observed that there is a great decrease in oxygen transmission rate as the percentage composition of the modified cellulose increases. It is obvious that modified cellulose played a powerful role in improving the oxygen gas barrier properties. The increased molecular interaction resulted in a film with compact structure and low OTR value. Oxygen Transmission Rate increases as the percentage of modified cellulose decreases because intermolecular bonding between fibre and matrices decreases. This resulted in a phase separation among the main components where the film could not be formed well, facilitating the oxygen permeation. So, it was more advantageous to improving the gas barrier properties by increasing the percentage of modified cellulose. This result indicates that the potential of these films to be used as a natural packaging to protect food stuffs from oxidation reactions.

Water Vapour Permeability Test

The water vapour permeability of films depends on many factors, such as the integrity of the film, the hydrophilic-hydrophobic ratio, the ratio between crystalline and amorphous zones and the polymeric chain mobility. We observed that there is a small decrease in water vapor trasmission rate as the percentage composition of the modified cellulose increases. This is because as the percentage composition of modified cellulose increases, hydrophilicity of the film decreases. This phenomenon could be related to the significant hydrogen bonding interaction with water. This result shows that these films may impede moisture transfer between the surrounding atmosphere and food, or between two components of a heterogeneous food product.

Mechanical properties

The prime consideration in determining the general utility of a polymer is its mechanical behavior, that is, its deformation and flow characteristics under stress. The mechanical behavior of a polymer can be characterized by its stress-strain properties.

It was observed that tensile strength and Young's modulus of films increases as the percentage composition of the modified cellulose increases. However, a decrease in elongation at break is observed as the percentage composition of modified cellulose increases. With the increasing of cellulose content, the interactions between the cellulose and the matrix is improved and crack propagation was inhibited, which resulted in the increased tensile strength and Young's modulus. Contrarily, it illustrated that there were interfacial adhesion between cellulose and the matrix; otherwise, it would result in premature composite failure because the reinforcing cellulose simply pulled out of the matrix without contributing to the strength or stiffness of the material.

Conclusions

Film composites produced by this method shows very good biodegradation behavior, which renders them advantageous in terms of environmental protection. Moisture absorption result shows that modified cellulose plays great role in increasing the composite properties such as mechanical properties, since as the proportion of modified cellulose increases water uptake by the film composite was less.OTR and WVTR test values shows that modified cellulose plays powerful role in increasing the gas barrier properties. The produced film composites possess higher tensile strength as the proportion of modified cellulose increases and higher elongation at break as the proportion of PVA increases. So modified cellulose plays vital role in increasing the tensile strength of film composites. The incorporation of cellulose fiber reinforced mechanically the films, with increasing the tensile strength, reducing the oxygen and water vapor permeabilities. Apart from that the films produced are transparent and this transparency indicates the good dispersion of fiber in to the matrices. These prominent properties could be exploited for several applications, such as in transparent functional packaging and biomedical applications.

LIST OF PUBLICATIONS

1. "Preparation and properties of biodegradable film composites using modified cellulose fibre-reinforced with PVA" **Sandeep S. Laxmeshwar**, Madhu Kumar. D. J., Viveka.S., Nagaraja. G. K.* *ISRN Polymer Science* (Vol. 2012, Article ID 154314, 8 pages).

2. "Preparation and properties of composites films from modified cellulose fibre-reinforced with PLA" **Sandeep S. Laxmeshwar**, Viveka.S., Madhu Kumar. D. J., Nagaraja. G. K.* *Der Pharma Chemica* (Vol. 4, Issue 1, 2012, 159-168).

3. “Preparation and characterization of modified cellulose fibre-reinforced Polypyrrolidone film composites” **Sandeep S. Laxmeshwar,** Viveka. S., Madhu Kumar. D. J., Nagaraja. G. K.* *Inventi Journal Pharm Tech* (Vol. 2012, Issue 2, ISSN 0976-3783).

4. “Preparation and characterization of modified cellulose fibre-reinforced polyvinyl alcohol/polypyrrolidone hybrid film composites” **Sandeep S. Laxmeshwar,** Viveka. S., Madhu Kumar. D. J., Dinesha, Bhajanthri. R.F, Nagaraja. G. K.* *Journal of Macromolecular Science, Part A* (Accepted).

5. “Effect of modified cellulose fibre on a biocomposites reinforced with PVA and PLA” **Sandeep S. Laxmeshwar**, Viveka. S., Madhu Kumar. D. J., Dinesha, Sunil. G. Rathod, Nagaraja. G. K.* *Journal of Plastic Film and Sheeting* (Communicated).
6. “Preparation and investigation of gas barrier, mechanical and biodegradable properties of hybrid film composites of modified cellulose - PVA/ PLA” **Sandeep S. Laxmeshwar**, Madhu Kumar. D. J., Viveka. S., Dinesha, Bhajanthri. R.F, Nagaraja.G.K.* *Advances in Materials Research* (Communicated).

CONFERENCES ATTENDED AND PAPERS PRESENTED

1. Presented Paper entitled “Mechanical, moisture absorption and biodegradation behaviours of modified cellulose reinforced with PVA biocomposites” at JC College, Polycon-2011, 5th National Conference on “***Plastic and Rubber Technology***” on 25-26th April 2011.

2. Presented Paper entitled “Modified cellulose fibre-reinforced with PVA and PLA hybrid biocomposites: barrier and mechanical properties” at Mangalore University, International Conference on “***Synthetic and Structural Chemistry***” on 8-10th December 2011.

3. Presented Paper entitled “Mechanical, moisture absorption, permeability and biodegradation behaviours of modified cellulose based bio-composite” at Jain University, Bangalore, One-Day National Conference On “***Recent Trends in Food Science & Nutrition Research***” on 15th December 2011.

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