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Use of Blend Technique for Adjustment of Biodegradable Cellulose Acetate to Fiber Applications

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Cellulose acetate is a semi-ordered polymer, used in various plastic applications. To adjust this biodegradable polymer to fiber application, the polymer is blended through its amorphous matrix with acrylonitrile copolymers to thermally support the polymer. The blending process, assisted with ultrasonic waves, led to the formation of a homogeneous matrix up to 25 % of the copolymers content. A unique glass transition temperature indicates the formation of new macromolecular matrix as a result of each blend sample. The results revealed that the blend samples exhibited higher thermal stability as shown from thermal analysis as compared to cellulose acetate. The mechanical properties were also greatly improved. Thus, blending cellulose acetate with the prepared copolymers enable it to withstand high temperature, which adjust it for fiber applications.

Keywords: Cellulose acetate, Mechanical properties, Polymer blends.

INTRODUCTION

Polymer blend is a method to mix two or more polymers physically or mechanically to reach a homogeneous blend. Thus, the blend is new polymeric material exhibiting new properties which differ from those of the homopolymers [1].

To obtain homogeneous system, high miscibility of the two homopolymers should occur. Sometimes the miscibility depends on the molecular contents of the blend and to which extent they will be miscible [2].

As examples of biodegradable polymers are cellulose and starch basic compounds [3] are extensively studied due to their low cost and high availability [4]. Blending cellulose with other polymers achieved optimized properties. Cellulose as polysaccharide biodegradable polymer is known to be insoluble in most solvents that is why it should be chemically treated for further use.

Cellulose is modified to form a semi crystalline cellulose acetate. This biodegradable polymer is soluble in most organic solvent and could withstand thermal degradation up to 250 °C, depending on the average molecular weight and the degree of acetylation [5]. This heat stability adjust the use of cellulose in the manufacture of membranes and plastic applications rather than fiber applications which necessite the thermal stability at high temperatures [6].

Hirotsu *et al.* [7] studied blends of polycaprolactone and cellulose acetate in different proportions and the influence of adding poly ethylene graft-glycidyl methacrylate (PE-g-GMA) as a compatibilizer.

Liu *et al.* [8] studied the effect of fabrication factors influencing the structures and morphologies of the chitosan and cellulose acetate blend hallow fibers as adsorptive membranes to achieve highly porous structures with different pore sizes through a wet spinning process.

Uesaka *et al.* [9] studied the blends of poly(butylenes succinate), cellulose acetate casted from chloroform. They obtained homogeneous blend film over a wide range of composition.

Since blending is always used to improve polymer properties, it is used to modify the physical and chemical structures of the macromolecular compounds [10-12]. Miscible polymer blend led to the formation of new material possessing completely different properties, than those of the two homopolymers which might possess better tensile strengh. However, complete miscibility between two homopolymers is hardly obtained. The miscibility is always related to the available amorphous parts in the polymer matrix.

Poly(acylonitrile) is a highly ordered polymer due to the ladder structure formed as a result of dipole-dipole interactions of nitrile groups, while cellulose acetate possesses more than 40 % of its marix as amorphous chains depending on the degree of acetylation. Thus, cellulose acetate was able to form miscible blends with several synthetic polymers having electron rich pendant group such as poly(4-vinyl pyridine) [13].

It had been reported that PAN-CA blend was immiscible. However, graft copolymerization of the former improved the homogenity and the stability of their blends.

To adjust PAN to the manufacture of fibers small amounts of amorphous polymer as vinyl polymer may be added to improve process ability and dye ability [14]. The PAN copolymers had been copolymerized with methyl methacrylate (MMA) and resulting solution blends of the two types of modified PAN with cellulose acetate showed partial miscibility.

In the present work, cellulose acetate will be blend with acrylonitrile-itaconimide copolymers, under the effect of ultrasonic waves. The copolymer exhibits considerable amorphous reogins due to the size of itaconimide moieties, which might enhance the miscibility of the blend. Furthermore, the excellent resistance of the copolymers against high temperatures [15] would give the extra thermal stability of the blend as compared to the homopolymer.

EXPERIMENTAL

Synthesis of polyacrylonitrile (PAN): Polyacrylonitrile is prepared using redox polymerization, using sodium bisulfite and potassium persulfate. White precipitate of polyacrylonitrile was obtained, which was filtered and dried in oven. The polymer is kept in dry desiccator for further use.

Synthesis of N-substituted (phenyl)itaconimides: Some phenyl itaconimides derivatives are prepared (Fig. 1) by the reaction of itaconic anhydride (1 mol) in chloroform with the corresponding primary amine (1 mol), in chloroform, to form the N-substituted phenyl itaconic acid. The later undergoes dehydration using acetic anhydride and fused sodium acetate for 1 h at 70 °C. The whole solution was precipitated in cold ethanol [16]. These monomers were recrystallized from aqueous methanol (Fig. 2). The purity of the monomers was checked by thin layer chromatography (TLC). Table-1 gives the melting point data of the N-substituted phenyl itaconimides derivatives.

Preparation of acrylonitrile copolymers: Acrylonitrile-itacomimide copolymers were prepared as follows.

Copolymerization of various ratios of AN and haloN-PhIM (XPhIM) monomers, was carried out in 50 wt % DMF at 70 °C for 8 h, under inert atmosphere. Azobisisobutylonitrile (AIBN) is used as initiator. The copolymer was precipitated

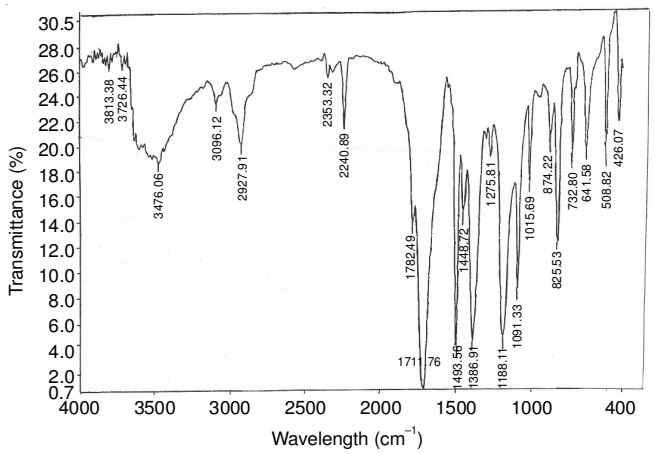

Fig. 1. FTIR spectrum of (AN/4ClPhIM) copolymer

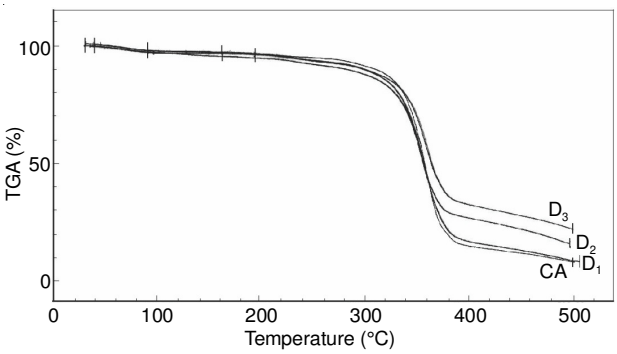

Fig. 2. Thermal behaviour of the CA/AN-3BrPhIM blend samples as compared to the standard cellulose acetate

TABLE-1
ABREVATIONS AND MELTING POINTS OF PREPARED ITACONIMIDES

Name	Abbrevation	m.p. (°C)
N-2-Chlorophenyl itaconimide	2ClPhIM	72
N-3-Chlorophenyl itaconimide	3ClPhIM	89
N-4-Chlorophenyl itaconimide	4ClPhIM	105
N-3-Bromophenyl itaconimide	3BrPhIM	104
N-4-Bromophenyl itaconimide	4BrPhIM	130

in cold methanol, washed with hot methanol using Soxhlet system for 40 h, filtered and dried under vacuum at 50 °C for 70 h.

Preparation of blend solution and films: The blend solutions were prepared by dissolving both the polymers in DMF. Allowing them to mix in ultrasonic bath to obtain homogeneous solution at 50 °C. The solution was cast on a dry and smooth glass plate. The glass plate was allowed to dry in vacuum oven at 40 °C and the blend film was obtained. The percentages of blend films compositions to be investigated are listed in Table-2.

TABLE-2
ABBREVIATION OF BLEND FILMS COMPOSITIONS

Blend film	Film compositions	Code name
CA/AN-2ClPhIM	95: 05	A1
CA/AN-2ClPhIM	85:05	A2
CA/AN-2ClPhIM	75:25	A3
CA/AN-3ClPhIM	95: 05	B1
CA/AN-3ClPhIM	85:15	B2
CA/AN-3ClPhIM	75:25	B3
CA/AN-4ClPhIM	95: 05	C1
CA/AN-4ClPhIM	85:15	C2
CA/AN-4ClPhiM	75:25	C3
CA/AN-4ClPhIM	50:50	C4
CA/AN-3BrPhIM	95: 05	D1
CA/AN-3BrPhIM	85:15	D2
CA/AN-3BrPhIM	75:25	D3
CA/AN-4BrPhIM	95: 05	E1
Ca/AN-4BrPhIM	85:15	E2
Ca/AN-4BrPhIM	75:25	E3
Ca/AN-4BrPhIM	50:50	E4

Spectroscopic measurements: FTIR (1650), the scanning range was from 4000-400 cm^{-1}.

Thermal properties: The thermal properies of the blend films was examined, under inert atmosphere, using a Perkin-Elmer (TGA/DTA) analyzer.

X-ray diffractometer (XRD): The spectral paterns were obtained using a Rigaku D/max 2500 v/pc X-ray diffractometer.

Mechanical properties: The tensile strength of the blend film was examined at room temperature using an Instron-type tensile testing machine (Testometric/M350-10KN ROCHOALL).

Morphology (ESEM): The surface investigation of the blend films occured using FEG-ESEM Q400 SEM.

RESULTS AND DISCUSSION

Characterization of produced materials: Acrylonitrile copolymer is characterized by FTIR. A clear identified peak is observed at 2240 cm^{-1} characterized for the nitrile group and absence of allylic double bond at 1660 cm^{-1} characterized the polymerization process (Fig. 1).

Thermal behaviour of cellulose acetate and the blend films were examined using TGA. It was previously known that the cellulose acetate starts to degrade at initial decomposition temperature, T_o = 250 °C, this value depends on the degree of acetylation as well as the average molecular weight of the polymer. In this work, the results of thermogravimetry of various compositions of CA/AN-3BrPhM, D1–D4, together with that of the cellulose acetate homopolymer showed that the initial decomposition temperature (T_o) of any blend sample is always higher than that of (cellulose acetate) (Fig. 2). Moreover, the total mass loss percentage, at high temperatures (500 °C), is always lower as compared to the homopolymer cellulose acetate, regardless of the composition ratio of the blend lm or the type of AN-XPhM copolymer (Table-3).

TABLE-3
PERCENTAGE OF MASS LOSS OF VARIOUS COMPOSITIONS OF CELLULOSE ACETATE/AN-BrPhIM BLEND FILMS

Blend film	Total mass loss % at 500 °C
Cellulose acetate	89.9
D1	85.7
D2	80
D3	75
D4	65
E1	69
E2	64
E3	58
E4	49

Furthermore, the blend of cellulose acetate with AN-4BrPhM, E1 to E4, lms possessed the lowest total mass loss % compared to all CA/AN-XPhM blend lms. This improvement in the thermal stability of the cellulose acetate blend lms is mainly attributed to the itaconimide moieties, which are known to possess high thermal stability [15]. The investigation by differential scanning calorimetry of blend films as compared to cellulose acetate and the value for T_g of each blend film was listed in Table-3. The

cellulose acetate homopolymer film exhibited an explicit glass transition at 240 °C. Only one T_g, close to that of cellulose acetate, was observed for all blend films (Table-4). The single T_g implied that the cellulose acetate was capable of forming a miscible binary blends with AN-XPhM.

TABLE-4
VALUES OF THE GLASS TRANSITION TEMPERATURE OF BLEND FILMS

Blend film	T_g (°C)
Cellulose acetate	240.0
C1	241.0
C2	242.0
C3	243.0
C4	243.5
E1	241.5
E2	242.5
E3	242.0
E4	243.0

The degree of compatibility depends on the content of the acrylonitrile copolymers. This is confirmed by the results given from the morphology of the blend films.

The surface morphology of cellulose acetate film and that of CA/AN-2ClPhIM, blend films are shown in Fig. 3 (A1, A2 and A3).

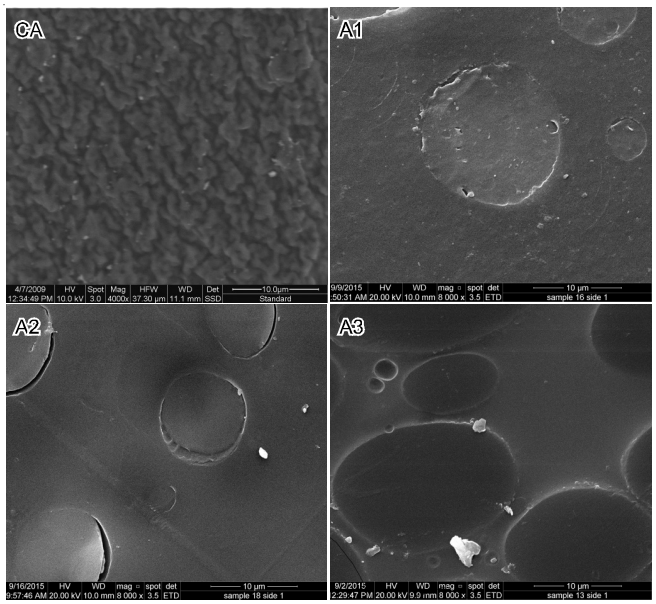

Fig. 3. Surface morphology of cellulose acetate film and that of CA/AN-4ClPhIM, blend films

The figure showed that the compatibility is slightly affected by the increase in the content of the acrylonitrile copolymer content. Thus, it was found that A3 (25 % copolymer) was slightly less compatible than A1 (5 % copolymer).

The data of Young's modulus at the break values of blend films of various compositions of CA/AN- 4 Cl PhIM as compared to the standard cellulose acetate film were listed in (Table-5). The results revealed that the elasticity of the films increased with the increase in the copolymer content in the blend film. Thus, the **C4** exhibited higher Young's modulus value than **C1**.

The crystalline structure of the plain cellulose acetate film and cellulose acetate/AN-4BrPhIM blend film was investigated using the X-ray diffractometer (Fig. 4). The results revealed that the blend film pattern exhibited a broad peak starting at diffraction angle (2θ = 18.7) and two sharp crystal peaks of diffraction angles at ($2\theta \leq 15$) corresponding to the crystalline

TABLE-5
VALUES OF YOUNG'S MODULUS (MPa) FOR VARIOUS COMPOSITIONS OF CA/AN-4ClPhIM BLEND FILMS

AN-4ClPhIM content/mass (%)	Young's modulus (MPa)
Cellulose acetate	1250
C1	1288
C2	1400
C3	1890
C4	2200

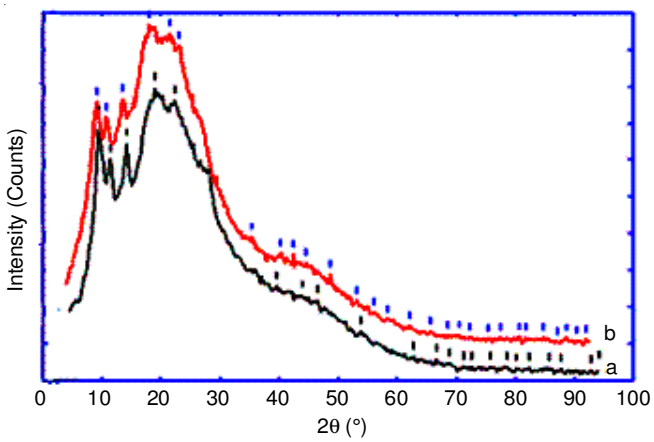

Fig. 4. X-ray diffractograms of CA/AN-BrXPhIM polymer blend (b) as compared to that of parent cellulose acetate (a)

region of cellulose acetate. Also, the peak related to acrylonitrile copolymer was observed as sharp one at (2θ = 17).

Conclusion

The ultrasonic waves enhanced the blending of cellulose acetate with acrylonitrile-itaconimide copolymers, which led to improvement of the thermal and mechanical properties.

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