

Poly(methyl methacrylate) modified Starch: their preparations, properties and applications

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Abstract

Plastic wastes are generally not easily degradable under the action of environmental components. They are very much resistant to microbial attack too. These non-biodegradable plastics accumulate over a longer period of time on earth leading to environmental pollution. However, this may be avoided by using biodegradable polymers. Thus the demand for the preparation of biodegradable polymers has grown up. In recent years, researchers have developed a few biodegradable polymers from renewable sources; those find a large application in the field of packaging, agriculture, and biomedical fields. Starch is one such biopolymer, modification of which may lead to a semi-synthetic polymer with good properties with an edge of biodegradability. Poly(methyl methacrylate) is a good modifying agent for such modification as revealed by the literature search. This review report summarizes the preparation of such poly(methyl methacrylate) grafted starch polymers via different physical and chemical methods, their properties, and their applications.

Keywords: *biopolymer, mechanical properties, poly(methyl methacrylate), starch.*

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1. Introduction

Synthetic polymers have become an invaluable gift to the mankind due to its importance^[1]. They have wide range of applications in almost every field of human activities like medical field, automotive, agriculture, food industry, packaging, etc^[2-4]. Among the various synthetic polymers, the demand for plastic is very high which has been used to manufacture millions of products. Its application as a packaging material has also been increasing day by day.

About more than 180 million tons of packaging materials are now being produced globally per year^[5]. Plastic materials are inexpensive and very much resistant to chemicals and other corrosive ingredients. Being non-biodegradable, they usually take up longer time to degrade under the influences of environmental components and hence possess serious threat to environment^[6,7]. The disposal process for the plastic waste is now a global concern. Therefore, a shift of strategy has been noticed in recent years. The number of publications of the keywords of the subject from 2012 to 2022 is shown in the Figure 1. All datas are taken from Google Scholar.

The industries are trying to minimize the production of plastic material from the petroleum resources^[8] rather working to develop a new material from the existing ones to incorporate biodegradable characteristics in it^[2,9]. Another strategy, which has also been adopted to solve this problem, is the recycling of waste. As per a published

report, the developed country like Japan is struggling to control the plastic waste. The Japanese Govt. has made a strategy to reduce 25% for single-use plastic waste and the reuse/recycling of 60% for plastic containers and packaging by 2030^[10]. So, there is an intense need for the development of materials, those will have comparable properties with the present day's polymeric materials and will be cheap and biodegradable in nature^[11,12]. This drives the idea to develop biopolymers from renewable resources which would degrade under the action of environment into smaller molecules (methane, CO₂ etc) and most importantly sooner than the traditional plastics^[12]. In past few years, scientists have successfully developed a few such biodegradable polymers from renewable sources like Chitosan, Cellulose, Guar gum, Chitin and Starch^[1,6,9,13-18]. These biodegradable polymers are now used in various applications including medical, industries and agriculture^[6,9]. However, high cost and low performance limit their wide use. Therefore, the development of new biodegradable polymers with enhanced properties and low costs have drawn interest of scientists and industries nowadays. Starch is a cheap and one of the most abundant biopolymers originated in nature. This material is greatly available for synthesis or fabrication to yield Starch-based polymeric materials for various potential applications^[1,17]. This review reports the salient features of methyl methacrylate modified Starch with special emphasis

on their preparations, characterizations, properties and applications.

2. Starch

Among all the naturally occurring biopolymers, Starch is the second most abundant^[19], renewable and cheap raw biomaterial^[7,17,19]. It is a polysaccharide with general formula $(C_6H_{10}O_5)_n$ ^[20,21]. It consists of a mixture of two polyglucans^[21], amylose [linear poly(1,4- α -D-glucopyranose)] and amylopectin [poly(1,4- α -D-glucopyranose) with (1,6- α -D-glucopyranose) as branching chains]^[21] (Figure S1). The shape of Starch granules can be spherical, oval, polygonal, dome-shaped, elongated-rod and their diameters vary from submicron to few 100 microns (Table 1)^[17,21,31]. Based on the chain length of amylopectin, the crystallinity of Starch granules varies and they exhibit A-, B- and C-type of X-ray pattern^[32]. The crystallinity of the native Starch varies in the range of 15% to 45%, implying that on an average 70% Starch is an amorphous material^[32]. Botanical originality of the Starch granules also defines its crystallinity, morphology, susceptibility to both chemical and enzymatic reactions. It is found that the variation of such properties as well structure is due to the variation in structure of amylose and amylopectin which are synthesized by different plants in different organs and at different stages of their development^[32-34]. Native Starch exists

in granular form having microscopic diameter ranging from 2-100 μm ^[32,33,35], comprising of macromolecules arranged in polycrystalline form^[32,33]. However, native Starch does not find much application due to its poor physico-mechanical property, poor water-resistance property, poor solubility and poor dimensional stability^[13,34,36]. Therefore, attempts have been made to modify Starch enzymatically, physically or chemically to enhance the scope of its applicability^[20,34]. Among the various ways of chemical modifications, grafting, cross-linking, esterification, etherification, oxidation are the few used very frequently for the modification of starch.

It is also possible to alter the physiochemical properties like biodegradability, biocompatibility, non-toxicity etc. via chemical modification^[23]. The hydroxyl groups present in the Starch molecule may be used for this purpose^[35]. Being biodegradable, biocompatible and non-toxic in nature, Starch has gained a lot of attention from the researchers^[24,37,38]. Starch can be treated with plasticizers to avoid the brittleness in the films and make it shatter resistant^[39,40]. However, the presence of plasticizer is not sufficient enough for application in packaging as Starch is hydrophilic in nature, therefore it is very much necessary to incorporate a hydrophobic group into it^[39,40]. Microorganisms such as fungi and bacteria consume Starch allowing easy degradation Starch-based polymer^[28].

3. Methyl Methacrylate (MMA)

MMA is an interesting monomer and can be easily polymerized to form resins and polymers. Among the different methacrylate monomers, methyl methacrylate (MMA) is the most commercially used monomer. It is capable to undergo polymerization by different polymerization methods^[41,42]. The homopolymer of MMA, poly(methyl methacrylate) (PMMA) finds many applications in various fields e.g., in drug delivery^[42], bone cement^[43], tissue engineering^[44], as electrolytes^[45], in molecule separation^[46], in conductive polymer matrix^[47,48], in photonic devices^[49], in solar devices^[47]. These diverse applications of PMMA are mainly due to its excellent optical transparency, biostability, processing

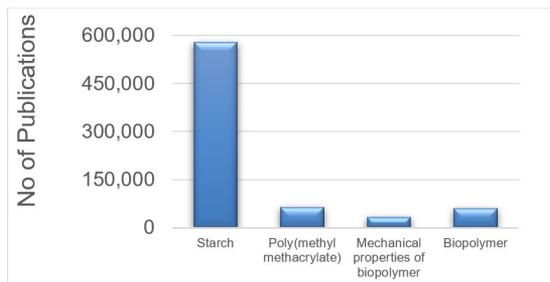


Figure 1. The number of publications in last 11 years based on the keywords search made of the subject.

Table 1. Size and shape of Starch granules with the amylose contents (%).

Starch	Diameter (μm)	Shapes	Amylose (%)
large canna Starch ^[22,23]	62 – 94	B-type, oval-shaped granules	38.7
medium canna Starch ^[22,23]	-----	oval and elliptical	-----
small canna Starch ^[22,23]	14-35	round and polygonal	29.2
small wheat Starch ^[24]	2–8	bimodal spherical shaped B-granules	23.0
large wheat Starch ^[24]	12-20	bimodal disc shaped A-granule	30.0
small potato granules ^[25]	5–20	spherical or ellipsoidal	212.5
medium potato granules ^[25]	25–40	ellipsoidal to irregular	250.8
large potato granules ^[25]	40–85	cuboidal	274.6
rice granules ^[26]	4.46-7.2	polygonal	29.7
Blackgram ^[27]	12.8-14.4	Round, elliptical, oval shaped	32.9-34.3
kidney bean ^[27]	15.5–60.5	Kidney shaped	35.9
large chick pea ^[27,28]	17 - 29	Spherical, oval shaped	30.2
small chick pea ^[28]	6 - 7	oval shaped	25.6
large maize granules ^[29]	5–20	spherical shaped	26.4
small maize granules ^[29]	>5	Angular-shaped	21.7
large barley Starch ^[30]	15-32	bimodal with large disk- shaped	24–29
small barley Starch ^[30]	2-3	bimodal	23 ~ 25

ability, very good weather resistance and good mechanical properties^[50]. Apart from these, MMA and PMMA are also used to modify the surface of fillers like Cellulose and Starch via grafting reaction.

4. Chemical Modification of Starch

4.1. Modification via conventional free radical polymerization

There have been many reports on the preparation of Starch graft copolymers. In most cases, conventional free radical polymerization (FRP) has been used for this purpose. For example, Çelik and Saçak^[36] described the azobisisobutyronitrile (AIBN)-initiated graft copolymerization of methyl methacrylate (MMA) with Starch. It was found that the grafting rate and grafting yield increased with increasing temperature^[36]. Shaikh and Lonikar^[16] reported the synthesis of Starch graft copolymer with a series of acrylic monomers- acrylic acid (AA), methacrylic acid (MA), and methyl methacrylate (MMA) by ceric ion initiation method for site-specific drug delivery. They reported that the efficiency of grafting increased initially, but later decreased with increase in the concentration of monomer except for MMA. They also studied the rate of release of paracetamol from a polymer blend and the grafted copolymer at two different pH, 1.2 and 7.4 respectively. They proposed that the prepared graft copolymer of Starch may be used for colon-targeted drug delivery. Sangramsingh et al.^[51] reported the preparation of Starch-g-PMMA using Ce (IV)-glucose as an initiator and the reaction mechanism is shown in the Scheme S1. They studied the effect of initiator concentration, amount of Starch, amount of monomer, temperature, time on the percentage of grafting. The activation energy calculated for this polymerization was also reported. The prepared graft copolymer was analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to evaluate their thermal properties. Pereira et al.^[52] detailed the graft co-polymerization of MMA and/or AA monomer with a blend of corn Starch/cellulose acetate by free radical polymerization. These monomers were polymerized at low temperature using benzoyl peroxide (BPO)/4-dimethylaminobenzyl alcohol redox initiator system to obtain the Starch/cellulose acetate based biodegradable hydrogel. Physical, mechanical and thermal properties of the prepared hydrogel were analyzed to check its applicability as an alternative material for bone cement or drug-delivery carrier in the biomedical field. In addition, they reported that the system follows Fickian-type diffusion but with an exception when AA is used in large amount. The mechanical properties of the hydrogel were found to be in the range of PMMA bone cements. Thus, they demonstrated the successful preparation of a degradable cement hydrogel with reasonably good mechanical behavior. Pimpan and Thothong^[53] reported the preparation of a PMMA grafted Starch copolymer in aqueous medium at 80 °C using benzoyl peroxide (BPO) as an initiator. The proposed mechanism for the polymerization is shown in Scheme S2. They also studied the effect of reaction time, amount of initiator, monomer and Starch on the grafting characteristics to obtain the optimum conditions for the best grafting result. Fourier transform infrared (FTIR) spectroscopy was used to study the grafting of Starch and

they tried to correlate these results with the morphological changes happened to the grafted Starch due to grafting using the Scanning Electron Microscope (SEM) analysis. Emulsion polymerization is one of the mostly employed polymerization technique for grafting of synthetic polymer onto biopolymers^[17]. It is also called as seeded polymerization since it allows the polymerization with larger size of molecules. There have been many reports on the preparation of Starch graft copolymer via emulsion polymerization using different kind of initiators. The mostly used initiators are ceric ammonium nitrate (CAN), ammonium persulfate (APS) and potassium persulfate (KPS). For example, Qudsieh et al.^[18] reported graft copolymerization of MMA onto sago Starch in emulsion using ceric ammonium nitrate (CAN) and potassium persulfate (KPS) as redox initiators as shown in Scheme S3^[17]. The grafting percentage was found to be maximized for CAN than KPS. Using the same initiator CAN, Li et al.^[54] detailed a classical study reporting the highest graft percentage (GP) of MMA onto Starch for the composition containing the maximum amount of MMA by weight. The group also reported the activation energy of thermal decomposition, crystallization behavior, thermal properties, morphology and biodegradation for the graft copolymers with different amount of grafting percentage. Horowitz Metzger and Broido methods were used to study the kinetics of thermal decomposition. Similarly, Ulu et al.^[19] described the synthesis of a Starch-based biodegradable and biocompatible (P(MAA-co-MMA)-Starch composite) carrier matrix for the immobilization of L-asparaginase (L-ASNase) using Starch as a doping particle. They prepared different compositions of P(MAA-co-MMA) copolymer using KPS as initiator. Different percentage of Starch (1, 3, 5 and 10 wt%) were doped in a particular copolymer composition and the enzyme L-ASNase was tried to immobilize. They confirmed the immobilization of L-ASNase by SEM, Energy Dispersive X-Ray (EDX) and Atomic Force Microscope (AFM)-mapping and determined the pH and thermal stability of both the L-ASNase and the immobilized L-ASNase. Mukherjee et al.^[55] detailed the synthesis of MMA grafted Starch copolymer in emulsion using KMnO₄-oxalic acid pair as redox initiator. They studied the effect of reaction time, reaction temperature and monomer concentration on the grafting of Starch. The highest percentage of grafting (49%) was reported at 50 °C for 3.72 cc concentration of monomer. The resultant grafted polymers were characterized by FT-IR, SEM, EDX and TGA analyses. Furthermore, they calculated the value of biodegradability and also studied the flammability of the prepared material by measuring the limiting oxygen index (LOI). In a similar manner, Ghosh and Paul^[56] reported the grafting of MMA onto Starch in methanol-water medium using potassium pervanadate as initiator under visible light. They studied the effect of reaction time, concentration of initiator and monomer, Starch contents and methanol-water ratios (v/v) on the grafting reaction. With this kind of variation, they achieved very good grafting results: percentage of grafting (95%), grafting efficiency (90%) and conversion (85%). Shi et al.^[15] prepared Starch-based graft polymers with four different methacrylate monomers: methyl, ethyl, butyl, and hexyl methacrylates and studied the variation of thermo plasticity and grafting parameters with increasing chain length of the alkyl ester groups. They confirmed the

successful preparation of Starch graft copolymers by ¹H Nuclear Magnetic Resonance (NMR), TGA and DSC analyses and reported that butyl methacrylate (BMA) grafted Starch gave the best thermoplastic film and exhibited better tensile properties. In a similar vein, Kisku and Swain^[57] described the synthesis of a biodegradable poly(methylmethacrylate)/Starch composite (PMMA/S). The prepared graft material exhibited good flame-retardant property. With Starch loading, they also observed a reduction of oxygen permeability through this composite, which enabled them to predict the potential applicability of this material in packaging industry. Qudsieh et al.^[31] employed the same initiator KPS and obtained the maximum graft percentage (90%) at an optimized reaction conditions with respect to monomer, reaction temperature, anhydroglucose units (AGU), potassium persulfate (PPS) and reaction period, which is shown in Scheme S4. They also calculated the viscosity average molecular weight of the grafted material by Huggin's and Mark Houwink's equations. Gao et al.^[58] detailed the graft copolymerization of MMA onto canna-Starch initiated by manganese pyrophosphate. They confirmed the grafting by FT-IR, SEM and XRD methods. They further reported the influence of concentrations of initiator, monomer, Starch, reaction time and temperature on the grafting percentage, grafting efficiency and grafting rate. From the experimental results, they established the rate equation which was equivalent to the equation derived from the proposed reaction mechanism (Scheme S5)^[58]. Imoto et al.^[59] reported the copolymerization of MMA with Starch in presence of Cu (II) ion of CuCl₂. Cu (II) ion forms complex with the Starch and water and it was confirmed by the measurement of difference spectrum and electric conductance of the Starch solution keeping CuCl₂ as the reference. In addition, they concluded with results that the polymerization proceeds in the hydrophobic phase that is micelle as formed by the Starch. Taghizadeh and Khosravy^[60] reported the graft polymerization of three different vinyl monomers such as acryl amide (AAm), acrylic acid (AA) and methyl methacrylate (MMA) onto Starch (S) using the redox initiator, potassium dichromate. They studied the effects of monomer, Starch, reaction temperature and initiator concentration on graft yield to obtain optimum conditions for the reaction. Bromometry titration was used to evaluate the kinetics data of grafting process. They obtained similar activation energies for the preparation of Starch-g-PAAm, Starch-g-PAA and Starch-g-PMMA. Li et al.^[54] reported the synthesis of a biocomposite by compounding PMMA grafted Starch with styrene-butadiene rubber (SBR). MMA and Starch were initially copolymerized via emulsion polymerization to prepare Starch-g-PMMA. The grafted copolymer was then compounded with SBR to obtain the composite. They studied the mechanical, morphological, biodegradable, swelling and water absorption properties of the prepared composite. The composites with Starch-g-PMMA loading at 10 and 30 phr exhibited good mechanical property. FE-SEM analysis and swelling test data supported this finding. The experimental results were found to be best fit in Halpin-Tsai model rather than Guth-Gold model they applied. The biodegradability of the biocomposite varies with immersion time and the Starch concentration as reported by them. Sekar et al.^[61] reported a comparative study of

physicochemical and mechanical properties of sheets of sago Starch (SGS) and MMA grafted Starch copolymer. The sago Starch (SGS) sheets were prepared in an aqueous medium containing ethylene glycol. The graft copolymer sheets were also prepared in the same media initiated by initiator potassium persulfate and sodium metabisulfite at 60 °C. The prepared sheets were characterized by FT-IR, SEM and EDX analyses. The tearing strength of SGS-g-PMMA sheets was found to be inferior than sago Starch sheets but tensile strength with elongation at break were comparable. The analysis of water absorption properties of SGS-g-PMMA sheets revealed that the sheet can be used for coating purpose as the sheet absorbed less water and so avoids further corrosion. The modification of Starch by conventional free radical polymerization as summary is shown in Table S1.

5. Modification Via Reversible-deactivation Radical Polymerization (RDRP)

5.1. Modification of Starch via its hydroxyl groups

Starch can be modified physically, chemically or enzymatically depending on the requirement as well as the end use. Chemical modification enables the addition of a functional group in the Starch moiety replacing its hydroxyl group. Due to this, Starch becomes an important material in industries^[62]. Chemically it can be modified by different chemical reactions such as esterification, etherification and oxidation^[34]. However, during modification of Starch, its granule form is maintained and only few hydroxyl groups are transformed to yield its ethers or esters^[63]. These hydroxyl groups of Starch can be modified to incorporate an initiating site for reversible-deactivation radical polymerizations (RDRP). For example, hydroxyl groups of Starch may be converted to groups containing an active halide bond which eventually may be used for grafting of monomers via atom transfer radical polymerization. In this case, the resulted modified Starch may be termed as macroinitiator. There have been several reports on the modification of Starch as a macroinitiator for a further modification or grafting process. The different chemical reagents used and the degree of substitution reported in this process are tabulated in Table 2.

6. Modification Starch as Macroinitiator

6.1. Via ATRP

In recent years, there are several reports on the Starch-initiated polymerization of different monomers by different RDRP among which atom transfer radical polymerization (ATRP) is mostly employed^[41]. ATRP is a well-controlled radical polymerization which allows copolymerization with controlled architecture^[34]. Bansal et al.^[20] prepared copolymers of MMA and styrene by SI-ATRP and AGET-ATRP using expanded corn Starch (ECS) as a support. They first converted the corn Starch into expanded corn Starch (ECS) then carried out SI-ATRP of MMA from the Starch surface. For this, Starch was modified as a macro-initiator (ECS-Br) by reacting few of its -OH groups with 2-bromoisobutryl bromide (BiBB). This ECS-Br was used for activator generated by electron transfer (AGET-ATRP) of MMA. ECS-Br was also used to prepare copolymers of MMA and styrene via SI-ATRP. They further determined the degree of substitution by NMR

Table 2. Synthesis of Starch macroinitiator and polymerization by different techniques of ATRP.

Preparation of macroinitiator					Polymerization condition	
Type of Starch	Reagents	Mole ratio in the Reaction ^a	Degree of substitution ^b (macroinitiator)	Technique	Temperature of reaction (°C)	Technique
Acetylated Starch ^[64]	2-bromoisobutyryl bromide	0.02	0.3	Substitution of hydroxyl group	70	ATRP
		0.09	1.0			
		0.76	3.9			
Expanded corn Starch ^[20] orn Starch ^[13]	Ethyl 2-bromoisobutyrate	-----	0.06	Substitution of hydroxyl group	70	SI-ATRP AGET-ATRP
		1.1	0.56			
		1.3	0.72			
		1.5	0.83			
		1.7	1.11			
		1.9	1.22			
		1.5	1.06			
		1.5	1.20			
		1.5	1.53			
		1.5	0.12			
		1.5	0.83			
		1.5	0.93			
		1.5	1.36			
Amylopectin ^[65]	Tert-butyl α -bromoisobutyrate	1:3	1.04	Substitution of hydroxyl group	20	ATRP
		1:3	1.08			
		1:3	0.98			

spectroscopy and found to be 0.06 and also characterized the polymers by SEM, FT-IR and ¹H NMR analyses. Wang et al.^[34] reported the synthesis of Starch-based copolymers (Starch-g-PS and Starch-g-PMMA) with styrene and MMA via ATRP. Starch was used as a macroinitiator in this grafting reaction. The Starch macroinitiator was prepared by esterification reaction with 2-bromoisobutyryl bromide (BiBB) in a solution of ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) and dimethylformamide (DMF). They further studied the effects of molar ratio of monomer to solvent, ligand, initiator and temperature on the graft polymerization. The prepared macroinitiator and the grafted copolymers were characterized by ¹H NMR, FT-IR and TGA analyses. Similarly, Nurmi et al.^[64] also reported the synthesis of Starch grafted copolymer of MMA with acetylated Starch via ATRP. Starch was used as a macroinitiator with varying densities and lengths in a controlled manner. They prepared it with different degree of substitution by the reaction of 2-bromoisobutyryl groups with the hydroxyl group of acetylated Starch. The graft polymerization was carried out in bulk as well as in tetrahydrofuran (THF) using CuBr/bpy as catalyst system. Furthermore, they studied the hydrophobicity of the prepared copolymer using contact angle measurements. In a similar vein, Handayani et al.^[65] modified amylopectin using tert-butyl α -bromoisobutyrate (TBBiB) to yield an efficient macroinitiator, Ap-TBBiB. This initiator was used to prepare amylopectin-g-PMMA through ATRP. The grafted copolymers had well-defined structure, as evident by different characterization techniques^[65].

6.2. Modification via NMP

Nitroxide mediated polymerization (NMP) can also be used for grafting from naturally occurring biopolymers. One of the advantages of this method is that there are no additional

steps required for the purification of polymer to remove metal catalyst, color or odor unlike polymerization methods like ATRP and RAFT^[62]. Cazotti et al.^[62] reported PMMA grafted Starch nanoparticles (SNPs) via NMP. The SNPs based macroinitiator was first prepared by modification with 4-vinylbenzyl chloride and an alkoxyamine. The monomer (MMA) was then grafted from the SNPs-macroinitiator via NMP. The successful synthesis of macroinitiator and the grafted SNPs were characterized by TGA and different spectroscopic techniques like FT-IR, ¹H NMR and elemental analysis (EA) (CHN mode)^[62].

6.3. Modification via other routes

Blending is a technique by which a new polymeric material may be developed from two or more different polymers. There are few reports on the development of such Starch-based polymer blends and also Starch based composite with the involvement of MMA as a component. Espigares et al.^[66] developed a partially biodegradable acrylic bone cement based on blend of Starch and cellulose acetate (SCA). Copolymer of MMA and AA was prepared via FRP to be used as bone cement for this purpose. They incorporated different percentages of hydroxyapatite to input the character of bone-bonding to the prepared bone cement and evaluated their curing characteristics, mechanical property, bioactivity, degree of hydration and degradation. Byun et al.^[67] reported a biodegradable film from corn Starch, polyvinyl alcohol (PVA), nano-sized poly(acrylamide-co-methyl methacrylate) (PAAm-co-MMA) and TiO₂/PAAm-co-MMA nanocomposite. They investigated the physical properties of the prepared films which also exhibited good photocatalytic degradability. Thakore et al.^[68] detailed the complete classical study of PMMA and Starch cinnamate (SCN) blends prepared in

different solvents. The prepared blends were found to be compatible with the solvents they used. The biodegradability study showed about 13% weight loss when SCN content was 30% in the blend. There are some reports which reported that the poly(methyl methacrylate) grafted Starch blended with natural rubber latex enhances the tensile strength of the blend^[24,69]. Baishya and Maji^[70] reported the synthesis of a bio-based composite of Starch and wood flour. Starch was modified first via grafting with MMA in water for this purpose and then mixed with pre-treated wood flour. They studied the effects of three cross-linkers glutaraldehyde (GA), dimethyloldihydroxyethyleneurea (DMDHEU), and N-methylol acrylamide (NMA) on the various properties of wood/Starch-g-PMMA composite. They concluded from their observations that the cross-linker DMDHEU with greater number of functional groups showed maximum interaction with wood and composite and here was an enhancement in the overall properties recorded for this cross-linker as compared to the other two GA and NMA. Boesel et al.^[71] fabricated a Starch-based bone cements using a hydrophilic matrix (a mixture of Starch/cellulose acetate blend and a copolymer of MMA and AA) and bioactive glass, MgO-SiO₂-3CaO.P₂O₅ as filler. The prepared material is partially degradable, bioactive and has good mechanical properties and hydrophilicity. Nakason et al.^[72] reported the grafting of PMMA with natural rubber (NR). The resultant graft copolymer (NR-g-PMMA) was then blended with cassava Starch (CS) and natural rubber air dry sheet (ADS) to prepare NR-g-PMMA/cassava Starch and NR-g-PMMA/ADS/cassava Starch blends. They studied the scorch time and cure time of the two-blend compound and reported that NR-g-PMMA–cassava Starch has longer scorch time and cure time compared to NR-g-PMMA–ADS–cassava Starch. Interestingly, for the blend containing more amount of CS showed an increment in torque, hardness and cure rate index, while the tensile strength, elongation at break and tear strength decreased, which is an evident that the Starch particles cannot support the stress transferred from a rigid cassava Starch–rubber interface and elastomeric phase. Maiti et al.^[73] reported the preparation of a resorcinol-formaldehyde cross-linked corn starch matrix based green composite reinforced with Saccharum spontaneum L grafted copolymers (with MMA, AAm, AN and AA). Thermal analysis of this composite showed an improvement in its stability. It was also found that the composites exhibited better physico-chemical and mechanical properties than the matrix. FTIR and NMR analyses supported the complete biodegradation of matrix and the composites. Among the different reinforced composites, Starch-g-PMMA based composite exhibited better tensile strength but Starch-g-poly (MMA + AA) based composite exhibited maximum compressive strength.

7. Characterization and Properties

The Starch-g-PMMA, prepared by different ways as explained in the above sections are characterized by various analytical techniques for structural elucidation and also to evaluate their thermal, physical and mechanical properties, morphological and biodegradable characteristics. This section focuses on some techniques those are often used for the

investigation of properties of poly(methyl methacrylate) grafted Starch. Among them, many are very much specific for the study of a particular property. Few such properties are also discussed in this section.

7.1. Study of chemical structure

The most commonly followed techniques to study the chemical structure of polymers are FTIR, ¹H NMR and ¹³C NMR. These spectroscopic techniques are generally used with specific motive to evaluate chemical structure and to know the presence of some special kind of interactions. A FT-IR spectrum is usually used to prove the formation of graft copolymer of Starch (Starch-g-PMMA). The major peak at around 3449 cm⁻¹ (varying with different samples in the range of 3300-3600 cm⁻¹) is attributed to the stretching vibrations of -OH bonds of Starch and the bands at 1736 cm⁻¹ (varying with different samples in the range of 1735-1750 cm⁻¹) and 2952 cm⁻¹ (varying with different samples in the range of 2652-2972 cm⁻¹) are attributed to the C=O and >OCH₃ groups of PMMA part. If modification on Starch is not happened at all, all -OH groups of Starch will exist and characteristic peaks for PMMA will be absent. The FT-IR spectrum also helps to conclude the presence of Starch backbone in the grafted copolymer. Like Qudsieh et al.^[18] compared the FTIR spectrum of the Starch-g-PMMA with the native Starch and native PMMA spectra for the confirmation of successful grafting of PMMA. The presence of the major peak at 3449.78 cm⁻¹ is attributed to the stretching frequency of hydroxyl groups. The peak at 1736.70 cm⁻¹ is assigned for C=O stretching. The peaks at 842.32 and 751.33 cm⁻¹ are due to the -CH₂CH₂- group and peaks at 3000.84 and 2952.95 cm⁻¹ are due to the >OCH₃ group of PMMA and >CH- part of the grafted PMMA.

FTIR spectroscopy also may be used for the confirmation of the preparation of Starch macroinitiator and Starch graft copolymer, when the grafting polymerization is carried out via ATRP or any of its modified versions. In ATRP, the Starch based macroinitiator is prepared first, and then this macroinitiator is used for the preparation of Starch-g-PMMA. In general, the modification of Starch is carried out via different chemical reactions e.g., esterification, etherification etc. The FTIR spectrum of macroinitiator shows a peak for C=O group of the initiator part in the range of 1900 to 1600 cm⁻¹ and shift in the band for O-H vibration (shifting varies with the type chemical reaction used for the modification of Starch) as a confirmation of successful preparation of macroinitiator via esterification. The presence of characteristic peaks for PMMA and Starch in the same FTIR spectrum confirms the successful preparation of the graft copolymer. Like Wang et al.^[34] confirmed the successful synthesis of Starch macroinitiator via an esterification reaction by FTIR analysis. In the FTIR spectrum of Starch macroinitiator, the intense peak at 1740 cm⁻¹ due to the C=O group and a shift in the peak from 3381 cm⁻¹ to 3433 cm⁻¹ for O-H vibration confirms the successful modification of Starch via an esterification reaction. Again, the presence of peaks at 3435 cm⁻¹, 1731 cm⁻¹ and 1384 cm⁻¹ in the FTIR spectrum of Starch-g-PMMA indicate the successful synthesis of PMMA grafted Starch copolymer^[14]. While FTIR confirms the formation of graft copolymer, ¹H NMR and ¹³C NMR gives information about the structure. The ¹H NMR and ¹³C NMR

spectroscopy are considered to be an effective technique for the characterization of grafted copolymers prepared by different RDRPs. For instance, Zhao et al.^[14] utilized NMR spectroscopy for the structural analysis of PMMA grafted onto Starch as well as the Starch macroinitiator. In the ¹H NMR spectra of Starch macroinitiator, the main peaks appeared in the range of 3.7–6.2 ppm and 1.7–2.2 ppm assigned to bromoisobutryl group (BiB) (varying with different samples depending on the chemical used for Starch modification) as well as anhydroglucose unit of Starch. However, in ¹³C NMR spectra, they observed shift in the peaks from 100 ppm to 96 ppm and 60 ppm to 65 ppm after esterification confirming the preparation of macroinitiator. They also analyzed Starch-g-PMMA using the ¹H NMR spectrum. They obtained peaks in the ranges 0.6–1.0 ppm, 1.6–2.1 ppm and 3.4–3.8 ppm for –CH₃, –CH₂– and –OCH₃ in PMMA chains. For an incomplete polymerization, the peaks for monomer will appear in the NMR spectrogram.

7.2. Study of microstructure and morphology

TEM and SEM are the two powerful microscopic techniques commonly employed to study the morphology of Starch grafted copolymer. SEM is a type of electron microscope which is used for studying the solid surface directly. It produces image by scanning the surface with focused beam of electrons. It gives information about the surface composition and topography. SEM technique is utilized by different researcher to study the morphology of surfaces at different stages to know the changes. For instance, as reported by Çelik and Saçak et al.^[36] the granular structure of Starch changes after graft copolymerization, which can be inferred from the SEM images. Similarly, Wang et al.^[34] also reported that the morphology changes from bulk to macroporous on modification of Starch to prepare Starch macroinitiator by esterification reaction. High resolution SEM

(FE-SEM) is also employed by some researchers to obtain clear image of the polymer surface with higher resolution. FE-SEM is a powerful technique which uses field emission gun for electron source and an in-lens detector provides the surface image with greater energy range. Li et al.^[17] studied the dispersion state of PMMA modified Starch in the SBR matrix using FE-SEM. They observed that in Starch/SBR biocomposites (MMA 0 phr), the size of the Starch remained same due to re-crystallization and re-gathering characteristics but with increasing concentration of MMA, the size reduced and also very clear tensile fracture surface was obtained. But with variation of the Starch concentration, different observations were obtained. It was reported that an increase of Starch concentration, Starch starts to agglomerate on the surface with particle size 1-10 µm and deteriorates the mechanical properties.

7.3. Thermal properties

The thermal property of PMMA grafted onto Starch is studied by TGA, DTA and DSC analyses. This study helps us to determine the thermal stability of the prepared graft copolymer. In Thermogravimetric analysis (TGA), the loss of weight versus increase in temperature is measured over time. While the other thermal properties, like fusion, crystallization and glass transition temperature, etc. are studied by Differential Scanning Calorimetry. For convenience, the values of reported thermal properties of Starch grafted copolymers are shown in Table 3. In general, the insertion of Starch in to PMMA results in the enhancement of thermal stability of the composites^[57]. The virgin Starch and the PMMA in general, degrades at lower temperature, however upon grafting, the degradation temperature of the Starch grafted copolymer is improved^[36].

Table 3. Thermal properties of Starch grafted copolymers.

Starch grafted copolymer	Polymerization method	TGA data								Reference
		Decomposition Temperature in °C at different stages				Weight loss in % corresponding to decomposition Temperature (°C) at different stages				
		1st	2nd	3rd	4th	1st	2nd	3rd	4th	
Starch	-----	35	165	420	-----	11.6	64.2	78	-----	[74]
PMMA	-----	203	297	400	-----	12	16	64	-----	[75]
Starch-g-PMMA	Solution FRP	300	600	-----	-----	-----	80	-----	-----	[11]
Starch-g-PMMA	Solution ATRP	150	-----	-----	-----	-----	-----	-----	-----	[18]
Starch-g-PMMA	Emulsion FRP	144	273	301	503	20	40	60	80	[19]
Starch -g- MMA (Crosslinked with wood flour by GA)		233	299	360	490	20	40	60	80	
Starch -g - MMA (Crosslinked with wood flour by NMA)		244	320	387	526	20	40	60	80	
Starch -g- MMA (Crosslinked with wood flour by DMDHEU)		286	338	391	558	20	40	60	80	
Starch -g-PMMA	Emulsion FRP	-----	600	-----	-----	54.5	89.2	-----	-----	[50]

For instance, Sangrainsingh et al.^[51] reported that the PMMA grafted Starch (30% PMMA) has better thermal stability than un-grafted Starch. This also indicates the successful preparation of PMMA grafted Starch^[19]. In some cases, the thermal stability of the grafted polymer does not show much difference with the Starch macroinitiator prepared or with the pristine Starch. This has also been observed that Starch-g-PMMA prepared via ATRP shows a three-stage thermal degradation, where the first degradation is due to the degradation of Starch-Br, while the other two are due to the PMMA part^[14].

7.4. Physico-mechanical properties

Since one of the primary reasons for grafting MMA onto Starch is to improve the mechanical performance of Starch, thus the mechanical properties are most concerned. It becomes important to optimize a balanced property between the toughness, strength and stiffness. The mechanical properties are characterized from different viewpoint. Several techniques are utilized to evaluate the graft copolymer for tensile strength, flexural strength, impact strength, fracture toughness, hardness, and so forth.

Tensile test is one of the most common methods carried out to learn about the mechanical strength of the Starch graft copolymer. The parameters tensile strength, Young's modulus and elongation at break are obtained from the tensile test. These parameters vary with the amount of Starch, along with the other factors like the method of Starch grafting or method of addition of Starch to the polymerization system, etc. Further, Compressive strength and wear resistance are also used to study the mechanical strength of the graft polymer. Baishya and Maji^[70] compared flexural and tensile strength of Starch grafted polymer composites containing different cross-linker (Table 4) and found that composites containing cross-linker DMDHEU exhibited highest flexural as well as tensile values. Yoon et al.^[4] reported an interesting fact about

the tensile strength of the Starch/PVA-PMMA-co-AM film prepared by Casting method. The tensile strength increased with increasing content of PMMA-co-AM nanoparticles but % of elongation was decreased. The films were prepared using different additives, but it was also observed in all the films that with increasing mole ratio of MMA in PMMA-co-AAm tensile strength is increased but % of elongation is decreased. However, the property of the film deteriorates when Starch, PVA, and only PMMA nanoparticle was used in the film. Shi et al.^[15], reported the tensile strength (Table 5) of films of grafted Starch with PMMA. On addition of 50% PMMA, the strength of the films varied from the earlier trend and was found to be increased by 10 times. However, the films had the highest strength with 100% addition of PMMA.

There are very few reports on the Hardness and Limiting Oxygen Index properties of PMMA grafted Starch copolymer. The crosslinkers which are used in the preparation of Starch based composite also enhances the hardness of the material. The wood Starch composite as explained in the above section was prepared by using three different crosslinkers namely GA, NMA and DMDHEU. The wood composite treated with DMDHEU showed maximum hardness followed by NMA- and GA-treated composites (Table 6).

The flame-retardant properties of polymer may be studied by the measurement of their Limiting oxygen index (LOI) value. LOI is the minimum concentration of oxygen in a mixture of N₂ and O₂, expressed as a percentage that will just support in combustion. This is a very important quantitative measurement of relative flammability of plastics used in aviation. Table 6 shows a considerable increase in LOI (from 44 to 56.5) when the crosslinker DMDHHEU was used for the preparation of the composite.

This change suggested that incorporating DMDHEU which acted as a binder as well as nitrogen provider significantly promoted the flame retardance of the composite^[70]. The flame-retardant characteristics of Starch/PMMA composite have

Table 4. Mechanical properties of few PMMA grafted Starch copolymers.

Starch grafted polymer	Flexural strength		Tensile strength (MPa)
	Strength (MPa)	Modulus (MPa)	
Starch -g- MMA (Crosslinked with wood flour by GA) ^[70]	30.8	2152	13.6
Starch -g - MMA (Crosslinked with wood flour by NMA) ^[71]	427	4369	14.8
Starch -g- MMA ^[70] (Crosslinked with wood flour by DMDHEU)	44.7	5011	15.6

Table 5. The tensile strength of both dry and wet Starch films grafted with PMMA^[15].

% homo polymer (PMMA)	Dry (breaking stress, MPa)	Wet (breaking stress, MPa)	Reference
0	0.23 ± 0.04	0	[15]
25	0.45 ± 0.01	0	[15]
50	2.9 ± 0.6	0	[15]
75	4.1 ± 0.5	0	[15]
100	12.8 ± 1.0	5.0±1.2	[15]

Table 6. Hardness and LOI properties of composites prepared using different crosslinkers^[70].

Starch Composite	Hardness (shore D)	LOI (%)	Reference
Starch -g- MMA (Crosslinked with wood flour by GA)	64.1 (±1)	44.5	[70]
Starch -g- MMA (Crosslinked with wood flour by NMA)	66.3 (±0.5)	50	[70]
Starch -g- MMA (Crosslinked with wood flour by DMDHEU)	72.0 (±1)	56.5	[70]

Table 7. Properties and potential applications of Starch-g-PMMA.

Starch grafted copolymer systems	Polymerization methods	Properties and Applications	References
Starch -g-PMMA-Br	SI-ATRP	Commodity plastic	[20]
Starch-g-PMMA	ATRP	Good thermal stability	[34]
Starch -g-PMMA	FRP	Thermoplastic film exhibits good tensile properties, thermal and water stability	[15]
Starch-g-PMMA	FRP	Enhanced thermal stability	[36]
Starch-g-PMMA	FRP then Compounding	Exhibited good mechanical properties	[54]
Starch-g-PMMA-SBR Composites		Enhanced water absorption and biodegradability	
Starch-g-PMMA	FRP	Surface coating agents for corrosion prevention	[61]
Starch nanoparticle-g-P(MMA-co-S)	NMP	Paper coatings, adhesives, and paints.	[62]
Starch-g-PMMA-latex	FRP	Enhanced tensile strength	[69]
Starch-g-P(MMA-co-BMA) -latex			
Starch-g-P(MMA-co-MA)-latex			
Starch -g-PMMA (Crosslinked with wood flour by GA, NMA and DMDHEU)	FRP then crosslinking	Good thermal stability Enhanced mechanical and viscoelastic properties, and water uptake resistances Improved flame-retardant property	[70]

also been reported^[57]. As per the report, an improvement in LOI was observed with the increase of Starch content in the Starch/PMMA composites. The LOI value of the composite gradually increased (from 28 to 47%) with increase in addition of Starch (upto 4%). This may be due to the reduction in heat release rate (HRR) and also, the chemical interaction between the OH group of Starch and the acrylic monomer MMA that greatly enhances the flammability.

8. Applications

The grafting of PMMA onto Starch not only alters the physical, mechanical and rheological properties but also incorporates some important and unique properties in the resultant grafted copolymer. The synthesis of common plastic with incorporation of biomaterial into it finds tremendous practical applications in medical field^[61], as films^[20,34], as plastics^[18], in packaging material^[7], in industrial applications including paper coatings, adhesives, paints^[62], thermoplastic product^[20], latex^[76] etc. In a recent development, scientists have reported a PMMA grafted Starch polymer which exhibits better properties than the commercially available bone cements^[66]. Preparation of Starch-based biodegradable hydrogels of MMA has also been reported which exhibits property similar to the property of PMMA bone cements^[61]. Not only as bone cements, Starch-based biodegradable graft polymers of MMA were also developed for other applications like carrier matrix for immobilization of the enzyme L-asparaginase^[19], material for wound dressing which is not degraded in water etc. PMMA grafted Starch also exhibits good flame retardant property and less oxygen permeability^[57]. Majority of plastic waste comprises of packaging materials which are mostly non-biodegradable synthetic polymers. In order to reduce such waste in environment, attempts have already been made to prepare Starch-based biodegradable polymers. There have been several reports on the preparation of Starch-based biodegradable polymers. Preparation of Starch-based biodegradable films of MMA with good physical and mechanical property was reported aiming to use the material in packaging^[7]. Starch-based biodegradable films of MMA was also prepared which

possesses good water stability and tensile properties^[17]. Even nanoparticles like nano-sized P(MMA-co-AAm) and TiO₂/P(MMA-co-AAm) were employed to develop such biodegradable films with good physical, mechanical and water resistance properties^[34]. In addition, rubber was also blended with Starch-based nanoparticle to enhance the property of the prepared biodegradable films^[69]. The applications and properties of PMMA grafted Starch are summarized in the Table 7.

9. Summary and Outlook

The PMMA grafted Starch copolymers exhibits good physical and mechanical properties. This copolymer has the potential to replace synthetic polymers from their traditional hold. Furthermore, Starch is a highly abundant and low cost naturally available biopolymer. Therefore, the resultant product will also be of low cost and will be beneficial for the consumers. The environmental pollution due the use of synthetic polymers also will be reduced to great extent with the use of such Starch based polymers in near future. Researchers are now focusing more to prepare biopolymer-based materials with the aim of complete replacement of the synthetic polymers. Many researchers have already reported the preparation of PMMA grafted Starch polymers with some good properties but there is always a scope for further improvement. Research in this line is under progress.

10. Author's Contribution

- **Conceptualization** – Dhruva Jyoti Haloi.
- **Data curation** – Dhruva Jyoti Haloi; Anjana Dhar.
- **Formal analysis** – Dhruva Jyoti Haloi; Anjana Dhar; Jayanta Barman; Hrishikesh Talukdar.
- **Funding acquisition** – DST SERB.
- **Investigation** – Dhruva Jyoti Haloi.
- **Methodology** – Dhruva Jyoti Haloi; Anjana Dhar.
- **Project administration** – Dhruva Jyoti Haloi.

- **Resources** – NA.
- **Software** –NA.
- **Supervision** – Dhruba Jyoti Haloi.
- **Validation** – Dhruba Jyoti Haloi.
- **Visualization** – Dhruba Jyoti Haloi; Anjana Dhar.
- **Writing – original draft** – Dhruba Jyoti Haloi; Anjana Dhar.
- **Writing – review & editing** – Dhruba Jyoti Haloi; Jayanta Barman; Hrishikesh Talukdar.

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Supplementary Material

Supplementary material accompanies this paper.

Figure S1. Structure of Starch.

Scheme S1. Schematic representation of polymerization reaction initiated by CAN initiator.

Scheme S2. Schematic representation of a) homopolymerization and b) graft copolymerization reaction initiated by BPO initiator.

Scheme S3. Schematic representation of copolymerization reaction of MMA and Starch initiated by CAN initiator.

Scheme S4. Sequence of steps involved in the graft copolymerization of MMA onto sago Starch initiated by KPS.

Scheme S5. Schematic representation of the proposed mechanism of complex formation among Cu(II) ion, water, MMA and Starch.

Table S1. Summary of modification of Starch via conventional free radical polymerization.

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