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REVIEW ARTICLE

pH-Sensitive Polymers with their Important Applications (A Review)

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Abstract: Materials that modify their chemical or physical characteristics in reaction to diverse stimuli, such as moisture, heat, water, or pH, are commonly known as smart materials or stimuli-responsive polymers. Typical applications for these polymers include catalysis, finishing, and coating processes. Tissue engineering, drug delivery, and gene transportation are additional applications that have emerged in the past two decades. As a result, their potential use extends to a wider range of applications, encompassing chemical processes, drug delivery, body-site targeting, separation, membrane activity, sensing and actuation, and agriculture. Recently, pH-responsive polymers have garnered considerable interest for implementation in membrane and 4D printing. The current review work encompasses previously published research through 2022, with a particular focus on the critical application of pH-sensitive polymers.

Keywords: pH-sensitive polymer, smart polymers, drug delivery, gene carrying, cancer treatment, biosensors.

1. INTRODUCTION

Polymers' exterior characteristics can be manipulated to modify their chemical, physical, and biological performance or conditions, thus boosting material biocompatibility. Therefore, academics are getting drawn to the discipline of stimuli-responsive polymers. These are the sorts of polymers that respond in both chemical and physical changes in their immediate environments. They are adept at recognizing every little alteration in their immediate surroundings, and they alter their responses accordingly. Temperature, solvent, salt ionic strength, light, magnetic field, electrical field, and pH are environmental variables. There are actually three kinds of environmental stimuli: 1) chemical, 2) physical, and 3) biological. Each kind of stimulus is offered in Fig. (1).

Polyelectrolytes react to changes in their surrounding by either accepting or donating protons from their environment to weak basic or acidic structures. It is acknowledged that these particular polyelectrolytes are pH-sensitive polymers [1,2]. The physical characteristics of pH-sensitive polymers could be altered by varying the charges on the polymer backbone. To produce pH-sensitive polymers, a variety of polymerization processes can be used, including group transfer polymerization, emulsion polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and conventional or controlled radical polymerization. Various structures such as homopolymers, block polymers, microgels, hydrogels (HGs), micro- and nanoparticles are used as pH-sensitive polymers [3]. Due to these responsive smart characteristics, these polymers have potential applications in the oil, coating, medical, and personal hygiene industries [4].

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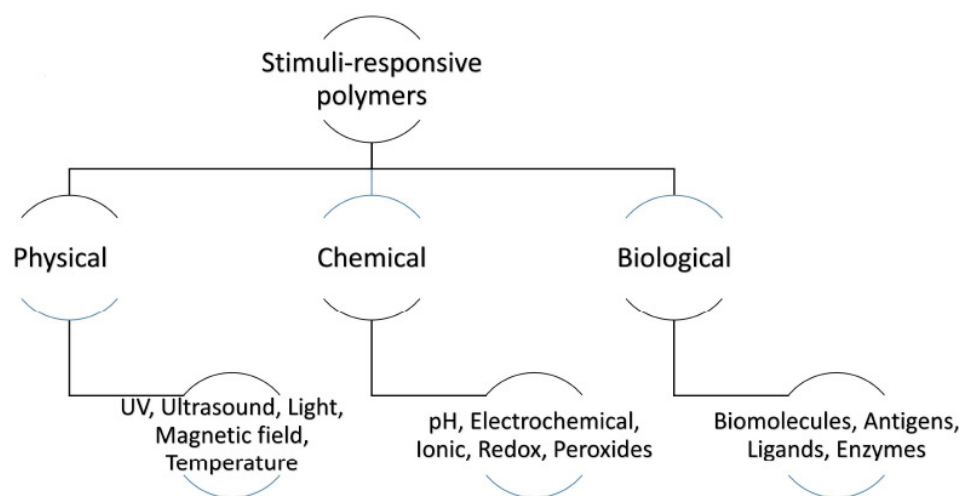


Fig. (1). Classification according to stimuli. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

In water or polar solvents, pH-sensitive polymers produce polymeric ions. These polymers expand when ionized in a polar solvent or water because the polymer chain repels the charge. When pH-sensitive polymers do not ionize, the polymers stay folded. Therefore, hydrophobic surface energy and electrostatic repulsion between charges determine how the polymers behave. As a result, these particular polymers propose conformational shifts that undergo slight environmental pH shifts [5,6]. The pH-sensitive polymer backbone contains weakly basic (like -NH_3) or acidic (like -COOH) groups that release or accept protons in response to changes in the surrounding pH (Fig. 2). For instance, polyacrylic acid (PAA), which ionizes at a pH higher than its pK_a value -COOH group – has a dissociation constant of 4.25, which causes the swelling of PAA due to the presence of electrostatic repulsion. Catalytic polymers exhibit the same opposite behaviour to the PAA swelling reaction. Lower pH causes them to ionize. As a result, pH-sensitive polymers exhibit reversible behaviour switching.

The acidic group found in polyacid polymers is unionized at low pH values. The swelling of the negatively charged polymers increases with a rise in the pH of polyacid polymers. It is precisely the opposite behaviour that polybasic polymers exhibit. Polybasic polymers swell as pH drops because the basic groups ionize [7-9]. pH-sensitive polymers are made from synthetic and natural materials with a sustainable conversation that needs to be

affordable and allow for future development. Additionally, covered are the sources, uses, and chemical characteristics of pH-sensitive polymers.

2. PH-SENSITIVE POLYMERS

Natural and synthetic polymers with viscoelastic properties and structures serve as the foundation for pH-sensitive polymers. The solubility, surface activity, and chain conformation all vary depending on the pH of the environment [6]. By organizing self-assembly, pH-responsive block copolymers change into gels, vesicles, swelled materials, and other structures [5]. The primary active groups in pH-responsive polymers are weakly acidic and weak basic groups located in their backbone. The degree of ionization of the ionic chain group indicates that a polyacid and poly base of pH-responsive polymers may be presented as per their backbone groups. The polyacid is in an expanded state at $\text{pH} > \text{pK}_a$, and the polybase collapses at $\text{pH} > \text{pK}_b$. Similar to how polyacid collapses at $\text{pH} < \text{pK}_a$ and polybase expands at $\text{pH} < \text{pK}_b$. The most frequently reported behaviors of these polyacids and polybases are swelling and deswelling. When charged and neutral, these polymers are typically soluble in water and insoluble in water, respectively. This results from the conversion of ionisable groups to neutrality, the elimination of electrostatic forces, and the predominance of hydrophobic interaction. Thus, the pK_a value is used to select pH-responsive polymers. Such polymers also depend on the pK_a (acidic ma-

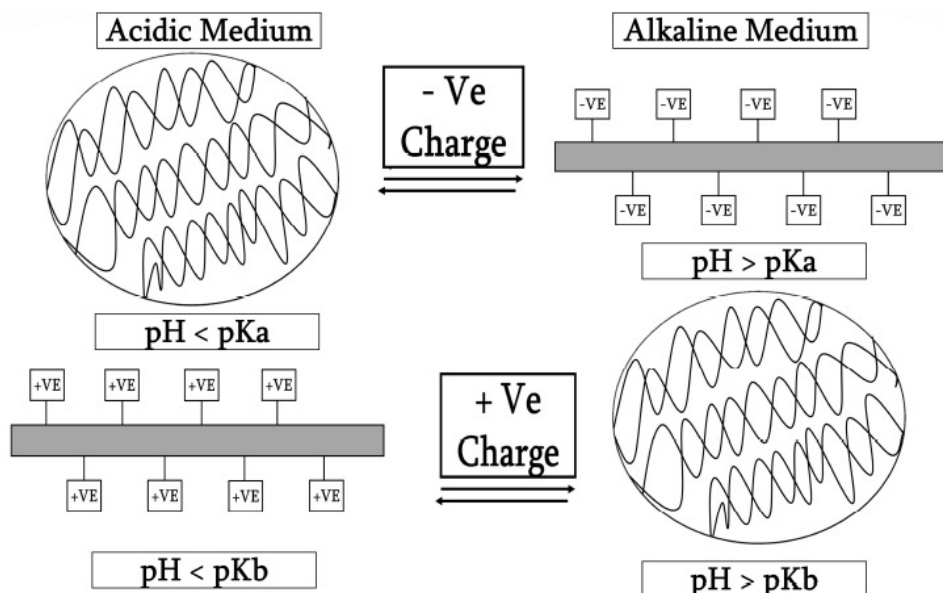


Fig. (2). Polymer state depending on the ionization. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

terial), and by altering the hydrophobic and electrostatic interactions, the pK (basic material) can be altered [7,8].

The two main categories of pH-responsive polymers (PRPs) are natural (Table 1) and synthetic (Figs. 3 and 4).

3. SYNTHESIS OF PH-SENSITIVE POLYMERS

The polymerisation techniques for synthesizing pH-sensitive polymers are controlled radical polymerization, emulsion polymerization, group transfer polymerization (GTP), and reversible addition-fragmentation chain transfer (RAFT). The polymers produced using the aforementioned techniques can have the following structures: homo- or copolymers, block copolymers, microgels, HGs, micro- or nanoparticles. Because of their use in oil/water separation, novel 3D materials with switchable wetting surfaces are receiving a lot of attention. Here, surface-initiated chain transfer radical polymerization is used to create a quick, pH-responsive, and incredibly effective melamine foam (MF) grafted with poly (2-dimethylaminoethyl methacrylate) [33].

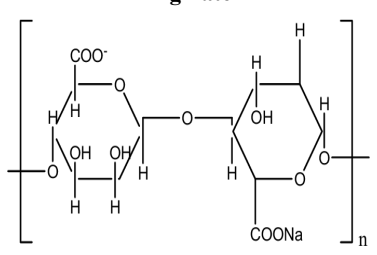
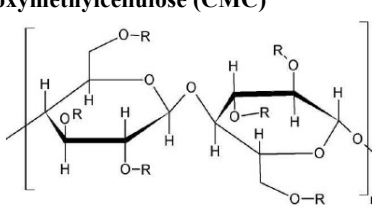
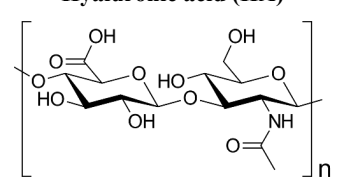
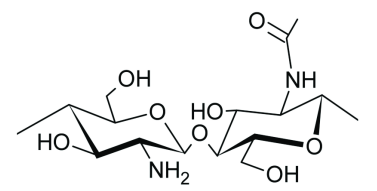
UCNPs@SiO₂@PAzo/MAA nanoparticles were synthesized using monofunctional 6-(4-methoxy-4'-oxygen-azobenzene) hexyl methacrylate (Azo) as a pH-responsive monomer and meth-

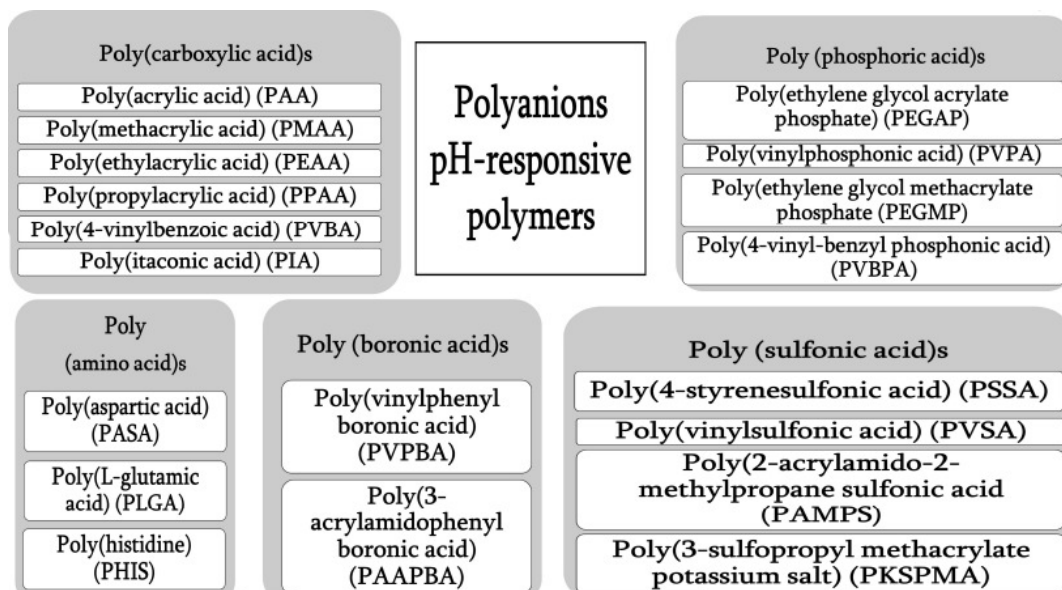
acrylic acid (MAA) as a photo-responsive monomer [34].

3.1. Emulsion Polymerisation

Emulsion polymerization is a commonly employed technique for producing pH-sensitive polymers based on vinyl. This method uses radical chain polymerization to create latexes from a narrow particle size distribution. Monomer(s), water, a water-soluble initiator, and a surfactant are needed for this polymerization. The primary disadvantage of this method is that it eliminates the surfactant that was used during polymerization, which could cause latex to coagulate or flocculate. The two subtypes of this method of polymerization are mini-emulsion and micro-emulsion. A surfactant-free method based on soft microgels (pickering emulsion) [35] was used to prepare new pH-sensitive polystyrene, PS, and poly(4-vinylpyridine), P4-VP, and nanospheres. These materials have the stimuli-responsive properties of micro gel and can be stabilized by Micking emulsions. Sterically-stabilized latexes with about 10% solids at pH 9 were produced by emulsion copolymerization of 2-(tert-butylamino)ethyl methacrylate at 70 °C in the presence of divinylbenzene (DVB) cross-linker and monomethoxy-capped poly(ethylene glycol) methacrylate (PEGMA) macromonomer [36].

Table 1. Natural pH-sensitive polymer.

Polymer	Details	References
Alginate 	- It is a polysaccharide. - Used in food, pharmaceuticals and medicine - It is a block copolymer of β-D-mannuronic (M) and α-L-guluronic acid (G) - It has pK_a value between 3 and 4 - Both monomer has carboxylic acid in its structure, and that is responsible for pH sensitivity - In presence of divalent cations, it shows mild gelling and swelling - At low pH, it shrinks and retained encapsulated molecules.	[9-15]
Carboxymethylcellulose (CMC) 	- It is an anionic cellulose derivative - Ionizable above pK_a 4.3 - Modified CMC-based hydrogels used for the control release of molecule - Used in agriculture, food, tissue engineering, and drug delivery	[16-20]
Hyaluronic acid (HA) 	- It is a compound of D-gulcuronic acid and N-acetyl-D-glucosamine disaccharide - At pH = 7, it acts as anionic polyelectrolyte - It has pK_a value between 3 and 4 - pH-sensitive HA nanoparticles used as protection for insulin against stomach's acidic pH. - Also, used in cancer treatment as cell surface maker	[21-25]
Chitosan 	- It is a polysaccharide with randomly distributed N-acetyl glucosamine (2-acetamido-2-deoxy-β-D-glucopyranose) and glucosamine (2-acetamido-2-deoxy-β-D-glucopyranose) - Application of chitosan is in medical fields, food, agriculture, wastewater treatment - It dissolve at low pH and remains insoluble at higher pH	[26-32]

**Fig. (3).** Polyanions PH responsive polymers.

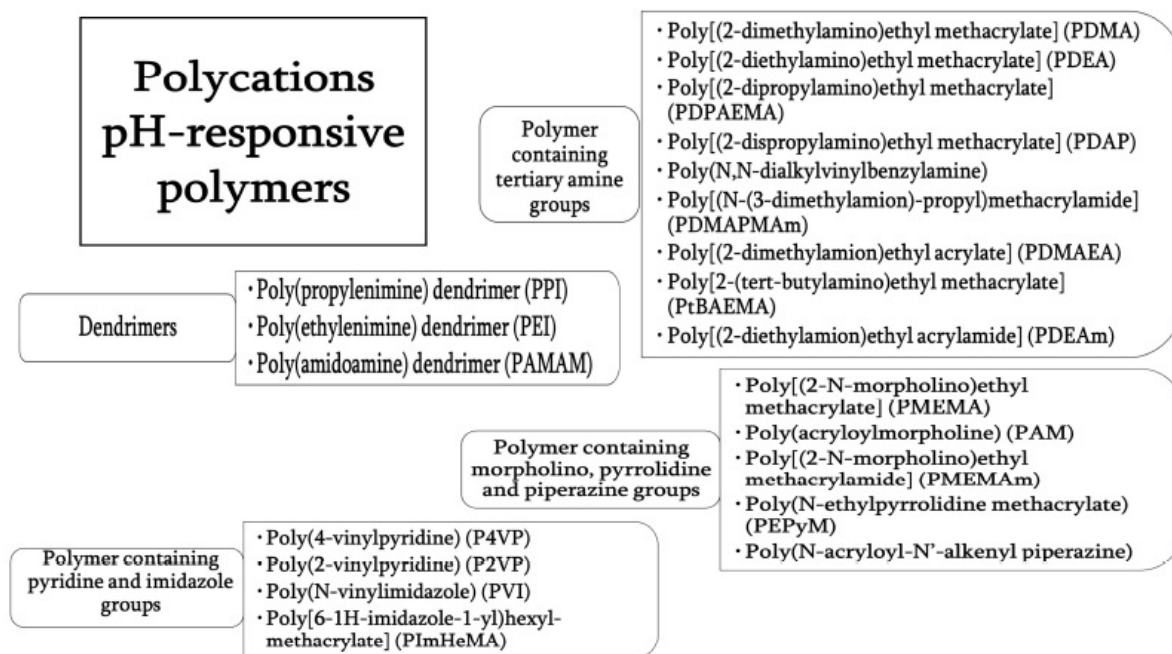


Fig. (4). Poly cations PH responsive polymers.

3.2. Group Transfer Polymerisation (GTP)

This method is mostly used in the synthesis of methacrylates. By transferring the silyl group to the added monomer and forming a new terminal group, Michael was able to add terminal silyl ketene acetal and monomer. Using a carboxylic acid salt as a catalyst, 1-methoxy-1-(trimethoxysiloxy)-2-methylpro-1-ene (MTS) was used as the initiator in this procedure. Block copolymer is created by the copolymerization of N,N-dimethylaminoethylmethacrylate (DMAEMA) with ethylene glycol dimethacrylate in tetrahydrofuran, where GTP controls the primary chain and molecular weight distribution [37]. As the chain growth stops with the aforementioned steps, block copolymers can also be created by adding a new monomer [38].

3.3. Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerisation

Reversible addition-fragmentation chain transfer (RAFT) polymerization has developed into a potent method for creating well-defined copolymer architectures during the past ten years. In particular, water-soluble, stimuli-responsive block, graft, and star copolymers have gained particular importance in the focused administration of medica-

tion and medical supplies. Protecting group chemistry is not usually necessary when RAFT polymerization is done directly in water at room temperature [39]. This polymerization process involves chain transfer, radical initiator, and monomer reactions to create polymers. This is the process of creating macromolecules with a low polydispersity index through the synthesis in which the radicals are produced by the techniques to initiate the polymerisation reaction. An RAFT agent helps maintain radicals at the end of the polymeric chain and aids in the chain's termination. Reversible addition-fragmentation chain transfer polymerization induced self-assembly (RAFT-PISA) was used to create the pH-responsive amphiphilic block copolymer micelles based on poly (2-(dimethylamino) ethyl methacrylate) (PDMAEMA) as a flexible corona and poly(hexafluorobutyl acrylate) (PHFBA) as a core [40]. Reversible addition-fragmentation chain transfer (RAFT) polymerization can be easily used to prepare benzaldehyde-functionalized amphiphilic block copolymers based on PEG-based oligo(ethylene glycol) methacrylate (OEGMA), benzaldehyde-containing para-formyl phenyl methacrylate (pFPMA), and pH-responsive 2-(diisopropyl)aminoethyl methacrylate (DPA) monomers. [41]. The reversible addition-fragmentation chain-transfer (RAFT) co-

polymerization of 2-propyl acrylic acid (PAA), 2-(dimethylamino) ethyl methacrylate (DMAEMA), and disulfide diacrylate (DSDA) using 4-cyano-4-((dodecylthio)carbonothioyl)thiopentanoic acid (CDCTPA) as RAFT agent and post-functionalization through bioconjugation techniques to synthesize novel folate-labelled pH-responsive hyperbranched polymers (HBPs) [42]. By employing a PEG-based benzoate-type RAFT agent to facilitate the RAFT polymerization of N-isopropylacrylamide and methacrylic acid monomers, a pentablock terpolymer with a core-shell-corona structure that is sharply responsive to pH and temperature was created [43]. Reversible addition-fragmentation chain transfer (RAFT) polymerization was used to create two different types of star polymers with a hydrophilic poly(2-hydroxyethyl acrylate) (PHEA) block combined with a PAA block on the inner or outer side of an arm chain [44].

3.4. Atom Transfer Radical Polymerisation (ATRP)

This method, known as controlled/living radical polymerization (CRP), polymerizes different vinyl and acrylic monomers under benign circumstanc-

es. In the ATRP process, an alkyl halide functions as an initiator and a transition metal in a reduced oxidation state as a catalyst. Using this method, formed radicals multiply and produce dormant sites, which reversibly deactivate them. The polymer chain can regrow by reactivating the same dormant sites. Using a low ppm level of CuBr₂/tris[2-(dimethylamino)ethyl]amine (Me6TREN) complex, photoinduced atom transfer radical polymerization (photoATRP) is used to create the thermo- and pH-responsive star-like block copolymers with controlled molecular weight and low dispersity [45]. PyMCIBMA monomer was subjected to reversible addition-fragmentation chain transfer (RAFT) polymerization in order to produce a well-defined poly (PyMCIBMA) homopolymer with an ATRP initiating group that contains Cl in each repeat unit [46].

Table 2 discusses some of the above techniques with examples.

4. STRUCTURES OF PH-SENSITIVE POLYMERS

Commonly described pH-sensitive polymers' structures are: linear homopolymer or copolymer,

Table 2. Synthesis of pH-sensitive polymers.

Technique	Details	References
Emulsion polymerisation	- Core-shell NPs containing a poly(methylmethacrylate) (PMMA) core and a P(MMA-co-EA) shell - System composed of PMAA and PDMAEMA - PAA NPs synthesizing with mini emulsion - Using water insoluble initiator with micro emulsion, such a polymer can also be prepared	[35, 47-51]
Group Transfer Polymerisation (GTP)	- Copolymerization of N,N-dimethylamino ethyl methacrylate (DMAEMA) or N,N-diethylamino ethyl methacrylate (DEAEMA) with ethylene glycol dimethacrylate (EGDMA) in tetrahydrofuran (THF) - Using tetrabutylammonium bibenzoate as a catalyst crosslinked polymer can be produced with various molecular weight	[52,53]
Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerisation	- Reducible PDMSEMSs were synthesized by RAFT polymerisation - Core-shell-like colloidal system generated for the delivery of drugs at weak acidic sites by RAFT - Polyethylene glycol grafted to poly(butyl acrylate) via RAFT agent, and poly(BA) core – poly(PEG-A) shell prepared for drug delivery	[39-44, 54, 55]
Atom Transfer Radical Polymerisation (ATRP)	- Copolymers of PEG and t-butyl methacrylate, iso-BA, n-BA or propyl methacrylate was prepared by ATRP - To enhance the drug delivery to solid tumor, PAA and Pluronic P85 block copolymers (P85PAA) was synthesized	[45, 46, 56, 57]

block copolymer, grafted copolymer, polymer brushes, star and dendritic polymers, NPs, and HGs (Fig. 5).

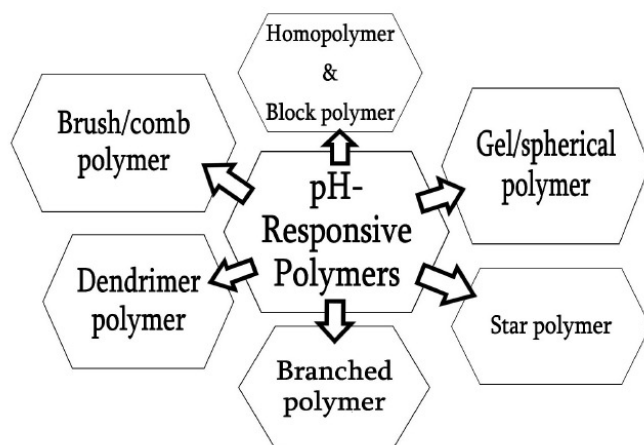


Fig. (5). Structures of PH responsive polymers.

4.1. Linear Copolymers

Linear copolymers include amphiphilic copolymers such as homopolymers and random copolymers. Two, three, or more monomers make up their structure [58, 59]. The micelle configuration is directly impacted by the soluble and insoluble segments found in the polymers. These kinds of polymers form micelle configurations in solution and self-assemble. Large numbers of ionized groups can be found in both the end and backbone of pH-sensitive copolymers [60]. Numerous variables, including pH, temperature, solvent properties, salt, and polymer concentration, have an impact on this assembly. With a change in pH, their structure takes on the forms of a worm, hollow, flower, and sphere [61].

4.2. Star Polymers

Micelle morphology of such polymers changes with the change in pH in star polymers. This polymer includes dendritic and highly branched copolymers or grafted polymers [61]. For drug delivery and coatings, this specific type of polymer is widely utilised. These polymers possess high solubility, modified thermal properties, and melt viscosities.

4.3. Hydrogels (HGs)

Hydrogels are insoluble structures that are cross-linked and extremely hydrophilic [62]. They have an absorption capacity of 10,000–20,000

times their dry weight. The acid/base linkage in these gels causes acidic groups to protonate at low pH values and basic groups to deprotonate at high pH values [63]. Anionic hydrogels ionized in solution ($\text{pH} > \text{pKa}$) will swell when pH is higher than the pKa value. On the other hand, the gel will swell when pH is less than the dissociation constant value ($\text{pH} < \text{pKa}$) because cationic groups are ionized [64].

4.4. pH-responsive Brush and Comb Copolymers

Copolymers of brushes and combs are made of hair-like chains that are grafted onto a surface. Physical absorption or chemical covalent formation binds brushes to the surfaces of polymers. Surface energy or state clearly exhibits modifications or changes as pH changes [61, 65].

5. APPLICATIONS

The pH value of certain tissues or subcellular compartments in the human body varies, including the gastrointestinal tract (Table 3). The pH is adjusted again within a narrow range by solvent or polymer-polymer contacts, indicating the extension and compaction of the polymer chain transition [66–68, 69]. Changes in the polymer's conformation can affect its surface wettability, solubility, and state of charge. Normal cells find the tumor microenvironment to be extremely acidic [70]. Therefore, PRPs can be used in cancer treatment to target specific tumor cells through the delivery of drugs or genes. The organ- or site approach is used to create pH-responsive drug delivery systems through the use of polymers with structurally ionisable groups. Using acid/base sensitive bonds to combine the polymers with the medication is an additional method for the same application. Here, the active molecule is released from polymers by breaking pH-sensitive linkages [71, 72]. Consequently, a wide range of bio-related fields, including drug delivery, chromatography, gene delivery, biosensors, and biotechnology, can benefit from the use of pH-sensitive polymers.

5.1. Drug Delivery

From the 1990s until the present, researchers have been interested in enteric coating as a colon

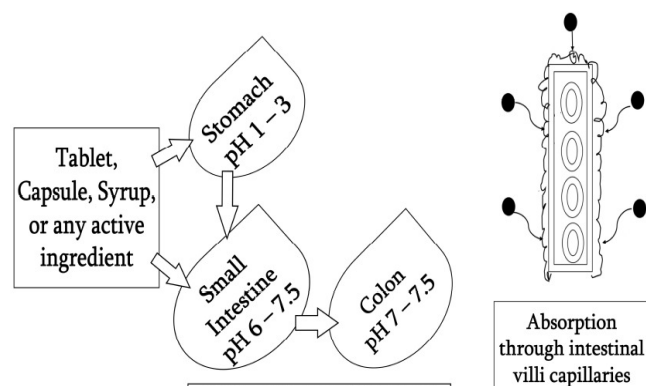
Table 3. pH values in various state in gastrointestinal tract [6,66,67].

Gastrointestinal Tract Zone	pH
Saliva	6.0 – 7.0
Blood	7.35 – 7.45
Stomach	1.0 – 3.0
Pancreatic fluid	8.0 – 8.3
Bile	7.8
Duodenum	4.8 – 8.2
Colon	7.0 – 7.5
Early endosome	6.0 – 6.5
Late endosome	5.0 – 6.0
Lysosome	4.5 – 5.0
Golgi	6.4
Vagina	3.8 – 4.5
Inflamed tissue	3.8 – 4.5
Tumor	6.5 – 7.2

delivery system. Enteric coating materials are primarily made of polymers called methyl methacrylate and acrylate. They can be used to deliver drugs orally with controlled and sustained release because it has been demonstrated that they increase drug stability [73, 74]. Coating agents, such as polymethacrylates with a pH of 6.0 to 7.0, are used to shield the drug core during transit through the intestinal and gastric zones (Fig. 6).

The tastes of drugs are altered by the bitter, sour, and salty properties of pH-responsive polycations, which react to extremely low stomach pH [67]. In contrast to them, pH-responsive anions stop the medication from being broken down in the stomach due to high intestinal pH.

The pH varies from 2 in the stomach to 6 in the colon and up to 8.2 in the lower duodenum, where pH-sensitive polymers are needed as a platform. Thus, researchers can create pH-sensitive carriers that release their contents in alkaline or neutral pH and remain stable in acidic pH based on changes in pH. Colon drug delivery is studied using a variety of polysaccharides, including locust bean gum, amylose, gaur gum, pectin, chitosan, inulin, cyclodextrin, and dextran. By creating pH-sensitive

**Fig. (6).** Drug carries out through GI-tract by PH responsive polymers. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

polymers, which are connected to virus particles, researchers have attempted to mimic living things (Table 4). Research has also been done on nanocapsules coated with pH-sensitive polymers, which use PAA as a carrier [67, 74].

5.2. Cancer Treatment

Drugs for cancer must be released into the acidic environment of the tumor [98]. Thus, ionizable pH-sensitive polymers designed for drug delivery are frequently employed in cancer therapy [99, 100]. Other anticancer drugs, such as oxaliplatin, which can deactivate in the blood, tumor selection, and lower bioavailability, pH-sensitive polymers, must be developed in order to treat the tumor tissue.

Differentiating cancerous cells from healthy cells is crucial when performing cancer surgery [101]. To detect malignant cells or tissues in MRIs, pH-sensitive polymers are employed as contrast agents in the form of micelles. When pH is less than 6.8, the micellar state is maintained by using a diblock copolymer poly(ethylene glycol)-poly(β -amino ester) loaded with Fe₃O₄. This micelle dissolves and ionized poly(β -amino ester) releases the Fe₃O₄ nanoparticles [102, 103]. The accuracy of the signal measurement is increased by their accumulation. Tetramethylrhodamine, a fluorescent dye, can also be incorporated with it.

The use of self-assembled amphiphilic copolymers as contrast agents in cancer treatments includes methoxy poly(ethylene glycol)-b-poly(L-histidine) and methoxy poly(ethylene glycol)-b-

Table 4. pH-sensitive polymers for specific drug delivery.

Types of Constitution	pH-sensitive polymer	Drug category	References
Tablet	• Methacrylic acid/ethyl cellulose • Hydroxypropyl methylcellulose	Antihistaminic	[75, 76]
	• Cellulose acetate phthalate	Anti-inflammatory	[77]
	• Cellulose acetate phthalate-co-poly(methacrylic acid)	Anti-inflammatory	[78]
	• Copolymer of methacrylic acid and methyl methacrylate	Anti-inflammatory	[79]
	• Nano-sized complex with chitosan (CH) and alginate (AL) as an oral vehicle for bursting release of protein at the target location to enhance the efficacy	Anti-inflammatory	[80]
Coated pellets	• NPs prepared with Methacrylic acid/ethyl cellulose and hydroxypropyl cellulose	Antihistaminic	[81]
	• NPs prepared with Methacrylic acid/ethyl cellulose and poly-acrylic resin	Anti-inflammatory	[82]
Microcapsules	• Copolymer of methacrylic acid and methyl methacrylate / Gelatine	Antihistaminic	[83]
	• Methyl cellulose/sodium alginate	Antihistaminic	[84]
	• Methacrylic acid/ethyl cellulose	Antihistaminic	[85]
	• Hydroxypropyl methylcellulose phthalate	Insulin	[86]
	• Methacrylic acid/ethyl cellulose and poly-acrylic resin	Insulin	[87, 88]
Hydrogel	• Sodium alginate/acrylic acid	Anti-inflammatory	[89]
	• Methacrylic acid (MAAc) • N,N – dimethyl amino ethyl methacrylate (DMAEMA)	Insulin	[90-92]
	• Kappa-carrageenan (KC)/guar gum (GG)/poly(vinyl alcohol) (PVA)-based pH-sensitive hydrogels	Anti-inflammatory	[93]
Nanoparticles	• Copolymer of methacrylic acid and methyl methacrylate and PLGA	Anti-inflammatory	[58]
	• polyethylene glycol diacrylate (PEGDA), N-vinylcaprolactam (NVCL), and 2-(dimethylamino) ethyl methacrylate (DMAEMA).	-	[94]
	• Chitosan	Insulin	[95]
Microgel	• Poly(2-isobutyl-acrylic acid)	Insulin	[96]
Solid lipid nanoparticles (SLN's)	• Ethyl cellulose/polyacrylic resin	Anti-inflammatory	[97]

poly(L-histidine)-diethylene-tri-amino-pent-acetic acid dianhydride-gandolinium chelate [104, 105]. The strategy for cancer therapy is shown in Fig. (7).

These polymers are used to create systems for diagnosing tumors. In contrast to MRI, pH-sensitive polymer micelles are used to target cancerous tissues. Chemotherapy for cancer treatment is aided by pH-sensitive polymers, which elimi-

nate the problem of multidrug resistance and poor tumor selectivity [106-108].

As a novel application, pH-sensitive polymers containing magnetic nanoparticles are also being considered for cancer treatment. Doxorubicin can be targeted to the cancer site in a magnetic field with the aid of Fe₂O₄ nanoparticles encapsulated in PLGA-coated chitosan [106-108].

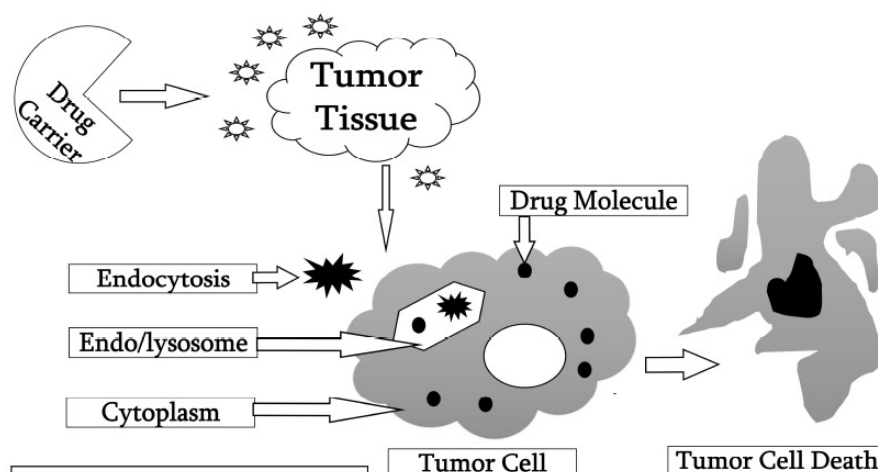


Fig. (7). Illustration of cancer therapy. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Table 5 lists the additional anticancer drugs that are used with polymeric carriers, which include paclitaxel, camptothacin, timixofen, and cisplatin.

5.3. Gene Delivery

Gene stability and cellular uptake are both low in the blood. To deliver nucleic acids for gene therapy, these must be overcome. Temperature, redox potential, enzyme-based structure, and extracellular and intracellular pH can all be used to achieve this [128]. Small interfering RNA and plasmid DNA are negatively charged nucleic acids that can be caged using a cationic polymer. DNA can interact electrostatically with polymers based on cationic tertiary amine methacrylate. The cationic polymer polyethyleneimine (PEI) [6, 129], which has a high transfection efficiency known as the "proton sponge effect," is primarily investigated for gene delivery. Negatively charged biomolecules condensed with cationic tertiary amine methacrylate-based block copolymers interact with the most promising gene delivery agent, poly[(2-diethylamino)ethyl methacrylate] [8, 53, 130], and are stable to proton sponge. Gene delivery is another application for PEG-modified cationic polymers (Table 6) [53,130-133].

5.4. Biosensors

In order to facilitate legible responses, colorimetric pH sensors—pH-sensitive polymers—that detect color changes have been developed. Rapid variations in biological adhesion to surfaces can be

identified through pH-sensitive zwitterionic polymers. Additionally, it can be used to identify gram-negative and gram-positive bacteria by looking for the formation of ionic complexes. In the context of discussing cancer treatment, pH-sensitive nanoprobe were also developed to respond in acidic environments. This helps to visualize tumors *in vivo* and determines their type and stage of development [139-142].

Based on pH-sensitive polymers, Park *et al.* prepared microspheres to function as microfluidic valves and replace traditional actuating parts [140]. Because pH-sensitive polymers swell and shrink in response to changes in pH, that valve opens and closes as per the condition of fluid either weak acidic or weak basic.

pH-sensitive polymers are widely used in the construction of insulin delivery systems for the treatment of diabetic patients. Insulin delivery requires precise dosing, making comparisons with alternative drug delivery methods challenging (Table 7). Reactive polymer produces self-regulating insulin in response to blood glucose levels, and it can regulate blood glucose levels within the recommended range [143].

5.5. Membranes

Much research has been done on environmental-responsive membranes (ERMs) for the use of PRPs in the membrane-related field. Graft polymerization of weak polyelectrolyte chains was

Table 5. pH-sensitive polymers for drug delivery (Cancer Treatment).

Types of Constitution	pH-sensitive Polymer	Anticancer Agent	References
Nanoparticles	• Chitosan/carboxymethyl chitosan (CM-CMCS)	Doxorubicin (DOX)	[109]
	• Polymethacrylic acid (PMAAc)		[110]
	• PEG-DOX-cur prodrug, acid-labile Schiff's base linkage		[111]
	• Chitosan coated nanoparticles		[106-108]
	• Chitosan	Tamixofen	[112]
	• Methoxy poly(ethylene glycol)-block-poly(glutamic acid) (mPEG-b-PLGA)	Cisplatin	[113]
Polymeric micelles	• Poly(L-histidine)	Doxorubicin (DOX)	[114]
	• PHEMA-b-PHIS		[115]
	• (HPMA)-hydrazone bonds		[116-117]
	• (HPMA)-benzoic-imine bonds		[118]
	• (PGE-pH-PBLG)-orthoester linkage		[119]
	• Poly(ethylene oxide)-b-poly(methacrylic acid) copolymer		[120]
	• Poly(ethylene glycol)-poly(lactic acid), hydrazine linker		[121]
	• PEG-b-PEYM, orthoester sidechains		[122]
	• Polyaspartic acid and PEG	Paclitaxel (PTX)	[123]
	• Poly[2-(dispropylamino)ethyl methacrylate]-poly[2-(methacryloyoxy)ethyl phosphorylcoline]	Paclitaxel (PTX)/ Tamixofen	[124]
	• Poly(β -amino ester)methyl ether poly(ethylene glycol)	Camptothacin	[103]
	• Poly(acrylic acid)-b-polycaprolactone	Gambogenic acid	[125]
Nanogel	• Poly(methacrylic acid)	Camptothacin	[126]
	• Poly(n-isopropyl acrylamide-methacrylic acid-hydroxy ethyl methacrylate)	Cisplatin	[127]

Table 6. pH-sensitive polymers for gene delivery.

pH-sensitive Polymer	Details	References
• Chitosan (cationic aminopolysaccharides)	Biocompatible DNA carrier	[134]
• Poly(ethylene glycol)-poly(aspartame hydrazinedoxorubician)	Polymeric micelle as nanocarriers for gene and drug delivery	[135]
• Liner or branched PEI • Polyamidoamine dendrimer • Poly(β -aminoester)	Gene transfection into vascular or cardiac cells	[136]
• Poly(N,N'-diethylamino ethyl methacrylate) and PLL sidechains	Polybase DNA carrier	[137]
• Polyethylenimine (PEI)	Cationic polymer shows proton sponge effect	[129]
• Poly(L-lysine)	High charge density and chian flexibility	[128]
• PEI and PMMA nanoparticles	For better diffusion in vascular system	[138]
• Poly[2-(diethylamino)-ethyl methacrylate] (PDEA)	Most promising nonviral vectors for gene delivery	[53, 130]
• Poly(ethylene glycol) and poly[2-(methacryloyoxy)ethyl phosphorylcoline]	Cationic nonviral vectors	[131-133]

Table 7. pH-sensitive polymers for biosensors.

pH-sensitive Polymer	Details	References
Sulfadimethoxine, N,N'-dimethylacrylamide and sucrose particles	A glucose sensitive hydrogel	[143]
2-hydroxy methacrylate and poly(ethylene glycol) acrylate with iron (II,III) oxide	A hydrogel for the delivery of anticancer drug	[144, 145]
Poly(N-isopropylacrylamide) with poly(diallyl dimethyl ammonium chloride) or poly(acrylic acid)	Multi-responsive flexible material, with potential application in soft robots, actuation, and sensing	[146, 147]
PDMA and PDMA-AM with sodium alginate	Environmental sensor on account of visible recognition	[148]
Poly(AAc-co-AAm)	Hydrogel muscle that swells and contracts in response to chemical signals	[149]

used to create such membranes [144-150, 151]. Poly(methacrylic acid) [150], poly[2-(diethyl amino) ethyl acrylamide] [151], or poly(acrylic acid) [152] had been grafted to prepare the membranes in which pH-respondent polymers were used to separate liquid from various mixture feeds. Hexadecane/water emulsion separation efficiency varies with pH; at 25°C, under alkaline conditions, separation efficiency is 97.10% [153]. Oil/water emulsion separation, the elimination of particular heavy metals from feed water streams, oil recovery, microfluidic devices, and wastewater treatment can all benefit from the use of pH-responsive ERM. Porous membranes based on poly(4-vinylpyridine) [154, 155] respond to pH variations by protonating and deprotonating internal pyridine groups, which causes the membranes to self-adjust in size. Additionally, it was proposed that membranes acted as porous microfiltration membranes by controlling water permeability.

5.6. 4D Printing

4D printing is commonly referred to as "3D printing plus time." The term "4D printing" refers to the process by which 3D printed materials can gradually change their forms, functions, and properties in response to specific stimuli such as water, light, heat, pH, and electricity. Because of this, products made using 4D printing have the ability to alter their shape in accordance with preprogrammed actions and needs. Thus, industries like biomedicine, soft robotics, flexible electronics, and food processing can benefit from 4D printing. [156]. It is necessary to compare the biocompatibility and biodegradability of to those of their syn-

thetic equivalents. Additionally, 4D printed pH-responsive hydrogels are worthy of being used in certain circumstances to release the medication in a particular area of the body under strict control [157, 158]. A new hydrogel with a hierarchical hydrogen bond system was created by You and his colleagues. It is made up of strong multiple hydrogen bonds between 2-ureido-4[1H]-pyrimidinone units and weak hydrogen bonds between N,N-dimethylacrylamides (DMAA) and acrylic acids (AAc). DIW can be used in conjunction with this crosslinking technique for 4D printing applications. [157, 158].

5.7. Smart Packaging Materials

In order to protect food from environmental factors and other factors like humidity, gases, and microorganisms, the manufactured product is typically packaged in packaging made of petroleum-based materials. With the growing concern over food safety, the packaging industry needs to use more natural resources in the materials that are used as packaging. Consequently, the newest technology in food packaging has been introduced: smart packaging based on biopolymers and natural colorants. These intelligent materials are also employed in colorimetric systems, which can alert customers to modifications in food quality and packaging conditions [159].

Using pH-sensitive polymers, clever packaging materials for food freshness monitoring have been proposed [160-162]. Antioxidant activity [163, 164], antimicrobial activity [165, 166], or both are present in this produced film.

5.8. Other Applications

PRPs are used for the aforementioned uses in a variety of purification and separation technologies, including electrophoresis, chromatography, and extractions [167]. pH-responsive hydrogels have been shown to rapidly adsorb or swell heavy metal ions. The heavy metal ions that are present in bovine serum albumin protein or the β blocker atenol are Pb^{2+} , Cd^{2+} , Ni^{2+} , Fe^{2+} , Cu^{2+} , Cr^{2+} , and Zn^{2+} . Both temperature and pH can regulate the interaction between the solute and stationary phase in chromatography, just as they can influence the separation of various biomolecules [168-172].

CONCLUSION

In the past 20 years, a lot of research has been conducted on pH-sensitive polymers because of their unique ability to adsorb to their surroundings quickly and reversibly by changing their structure and characteristics. Within this review, PRPs were the main focus; a source-based categorization of synthetic and natural polymers that are sensitive to pH and are referred to as polyacids and polybases. In addition to acting as biosensors, these polymers support functionality in the delivery of drugs, genes, and cancer treatments. Nevertheless, they interact with the substrate and frequently change its surface. PRPs come in a variety of structures, including gel, spherical micelle, brush, comb, block polymer, homopolymer, and dendrimer. They can be made by GTP, ATRP, RAFT polymerization, and emulsion polymerization. They can generally mimic the variations in pH found in the surrounding environment.

As consumer awareness of packaging products rises, smart packaging materials have recently been covered by the packaging industries as well. Thus, more materials for packaging that can withstand outside agencies and safeguard the products inside will be needed in the future. They also need to be biodegradable.

4D bioprinting will be used as the next generation of fabrication platforms for medical devices, hard and soft tissue structures, and dynamic adaptation, which can be accomplished by employing different stimuli-responsive materials, particularly hydrogels and shape memory polymers (SMPs), which have advantageous biomechanical proper-

ties. The 4D printing community has been working hard over the past few years to create innovative stimuli-responsive polymeric materials while keeping a biomedical perspective in mind [173]. With the advent of shape memory polymer composites (SMPCs), 4D printing and pH-responsive polymeric materials have drawn the attention of scientific scholars in large numbers in recent years. The 4DP feature of SMPCs facilitates the investigation of a wide range of engineering applications, such as wearable electronics, biomedical devices, automotive, food, soft robotics, and smart textiles [174].

In the future, researchers can examine drug delivery systems that respond to multiple stimuli, the ease with which sensitive polymers can be produced *via* synthetic routes, and the feasibility of doing so economically.

LIST OF ABBREVIATIONS

ATRP	=	Atom Transfer Radical Polymerization
RAFT	=	Reversible Addition-fragmentation Chain Transfer
SMPCs	=	Shape Memory Polymer Composites
ERMs	=	Environmental-responsive Membranes
AAc	=	Acrylic Acids

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RESEARCH

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Designing pH-responsive SAP-coated menstrual pads and comparing them to marketable products through quality analysis

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Abstract

Background For a specific purpose involving the pH of menstrual blood and the pH of the vagina during menstruation, the current work describes the development of pH-responsive superadsorbent polymer (SAP)-coated menstrual pads. Acrylic acid (AA) and methyl methacrylate (MMA) were used to create a pH-responsive polymer, which was then applied layer by layer to sanitary napkins. Using FTIR, the chemical composition and structure were examined. By examining tests for absorbent capacity, swelling capacity, water retention, sorption under load, strike through, wicking height, and re-wetness under load, the performance studies of coated pads were contrasted with those of menstrual pads that are sold commercially. Additionally, the coated pad's pH response was examined to determine how stable the polymer was against pH variation.

Results The use of SAP in this study resulted in a higher free swelling capacity (102.22 g/g) for tap water and absorption under load in sanitary napkins. The absorption capacity of SAP ranges from 8 to 24 h, with values ranging from 14.84 to 132.41 g/g. Similarly, wet back and striking through analysis indicated superior outcomes in comparison with commercial products. The pH of the prepared SAP helps to maintain the necessary acidity level (pH 3.02) for the vagina during menstruation.

Conclusions Based on comparison results from FTIR, absorbency capacity, rewet, strike-through, and pH, the report recommends using the pH-responsive SAP to coat the top layer of feminine napkins.

Keywords pH-responsive polymer, Superadsorbent polymer, Layer-by-layer, Menstrual pad, Absorbency

Background

Women experience menstruation every 21–28 days, lasting for a total of five days in each menstrual cycle. Menstruation is an essential process in the female reproductive system (Shibly et al. 2021; Woeller & Hochwalt 2015). Menstrual cycles typically span from three to seven days for females aged eleven to fifty. The mean blood loss during a menstrual cycle is 35 ml (ml), with

blood losses ranging from 10 to 80 ml (ml) considered within the normal range. The flow rate during the early menstrual day starts off high and gradually decreases from the second day of the cycle until the final few days (Nyoni et al. 2014). Menstrual fluid consists of approximately 50–60% blood, as well as mucous materials, secretions from the uterus, cervix, and vagina (Bae et al. 2018; Chakwana & Nkiwane 2014).

Women across different social strata in developing countries lack sufficient understanding of menstrual hygiene management, resulting in reduced productivity due to frequent school absences, infections, and other health issues that specifically impact women. Additionally, this lack of knowledge leads to feelings of embarrassment and hinders women's ability to engage in work.

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Economically disadvantaged and unconscious women often resort to unsanitary cloths for the purpose of collecting and retaining menstrual fluids. In addition, impoverished women, who are unaccustomed to wearing underwear, are not inclined to use commercial sanitary napkins, which require the use of panties or other types of undergarments. There is a necessity to create a hygienic sanitary napkin that is cost-effective and eco-friendly due to limited knowledge, expensive production, and the current socio-economic framework. Today's health-conscious women utilize a variety of products such as tampons, menstrual cloth pads, sanitary pads, and pantyliners. The menstrual cloth pad consists of three primary layers: the top sheet, which is responsible for direct contact with the body; the absorbing core, composed of materials designed to absorb menstrual flow; and the leaking barrier sheet, which prevents any leakage (Elsherbiny et al. 2022; G et al. 2020; Haider et al. 2023; Yadav et al. 2016).

The work presented focuses on the synthesis of a superabsorbent polymer (SAP) using methyl methacrylate and acrylic acid monomers. This polymer, known as poly(methyl methacrylate-co-acrylic acid) or poly(MMA-co-AA), exhibits pH-responsive properties. The synthesized polymer was applied to the uppermost layer of the sanitary napkin using a layer-by-layer technique. The performance of the coated napkin was evaluated by comparing it to commercially available products.

Methods

Materials

Acrylic acid (AA), methyl methacrylate (MMA), and benzoyl peroxide (BP) were obtained from A. B. Enterprise, Mumbai. Nitrogen gas and liquor ammonia were obtained from Madhu Chemicals (Mumbai), Sunshine Industrial Gas (Ahmedabad), Suvidhi Industry (Vapi), respectively. All the reagents used in the work are of analytical grade, so they are used directly as received without supplementary refinement.

Preparation of pH-responsive polymer

The apparatus comprises a 1000-ml capacity five-necked round-bottom flask with a double-helical parallel impeller agitator, thermometer, additive funnel, nitrogen gas inlet tube, and water condenser attached. Transfer 200 ml of a solvent mixture into the flask and add two small porcelain chips. After gradually heating the solvent mixture to 40 °C, pass nitrogen gas through the flask to remove any remaining air. A constant stream of nitrogen gas is used to add the 50 ml of monomer feed which consists of a solvent mixture, monomers, and cross-linker (Table 1)—dropwise at a rate of 3.0 ml/min into the additive funnel as suggested in Table 2. In order to start the polymerization, 0.01 percent

Table 1 Components for polymerization

Monomers	Monomer-a = Methyl Methacrylate and Monomer-b = Acrylic Acid
Solvent system	Solvent-I = Toluene and Solvent-II = Ethyl Acetate (solvent mixture of I:II is 60:40)
Cross-linker	Triallylamine, Triallylphosphite in equal proportions
Initiator	Benzoyl peroxide
Inhibitor	Tert-butyl hydroperoxide (TBHP)

of an initiator is added at the same time, and the temperature is progressively raised to 80 °C. Two hundred milliliters of the remaining monomer feed is added dropwise over the course of 1.5 h after the initial 50 ml of monomer feed has been added. Throughout the entire polymerization process, the temperature is kept between 80 and 90 °C. The polymerization reaction suggested in Fig. 1 is inhibited by adding a 0.01 percent inhibitor at the end of the reaction.

Characterization

The chemical structure and composition of pH-responsive microcapsules were examined using the PerkinElmer SpectrumTM 3 FTIR spectrometer, which is capable of performing Fourier transform infrared spectroscopy (FTIR).

Application on sanitary napkin

The top layer of the sanitary napkin was immersed in 20 g of pH-responsive dispersion and then padded through a two-bowl padding mangle as shown in Fig. 2. Again, the padded layer was passed through the SAP dispersion and padded. The process is repeated three times to generate a layer of SAP on top of the sanitary napkin. The samples for all prepared SAPs were coated by the layer-by-layer technique. Finally, all layered samples were baked at 82 °C for 3 min.

Free swell capacity (FSC)

This test outcome indicates how much distilled water the sample absorbs when it is fully swollen. The tea-bag method is the most expedient and convenient choice for samples with low quantities (W_0). The sample was prepared, placed into a teabag, and submerged in water or a saline solution for an hour. The tea bag was weighed again (W_1), and its swelling capacity was computed after it had fully swelled (EDANA 2019c; Qin 2016).

$$FSC = \frac{(W_1 - W_0)}{W_0} \quad (1)$$

Absorption under load (AUL)

AUL measures the fluid absorption capacity of SAP samples under specific pressure conditions. An SAP

Table 2 Components and amounts are set forth for polymers

Experiment	Monomer (g)		Cross-linker (g)	Solvent (ml)		Temperature (°C)
	a	b		I	II	
SAP1	80	20	0.01	240	160	80 – 90
SAP2	70	30	0.01	240	160	80 – 90
SAP3	60	40	0.01	240	160	80 – 90
SAP4	50	50	0.01	240	160	80 – 90
SAP5	40	60	0.01	240	160	80 – 90

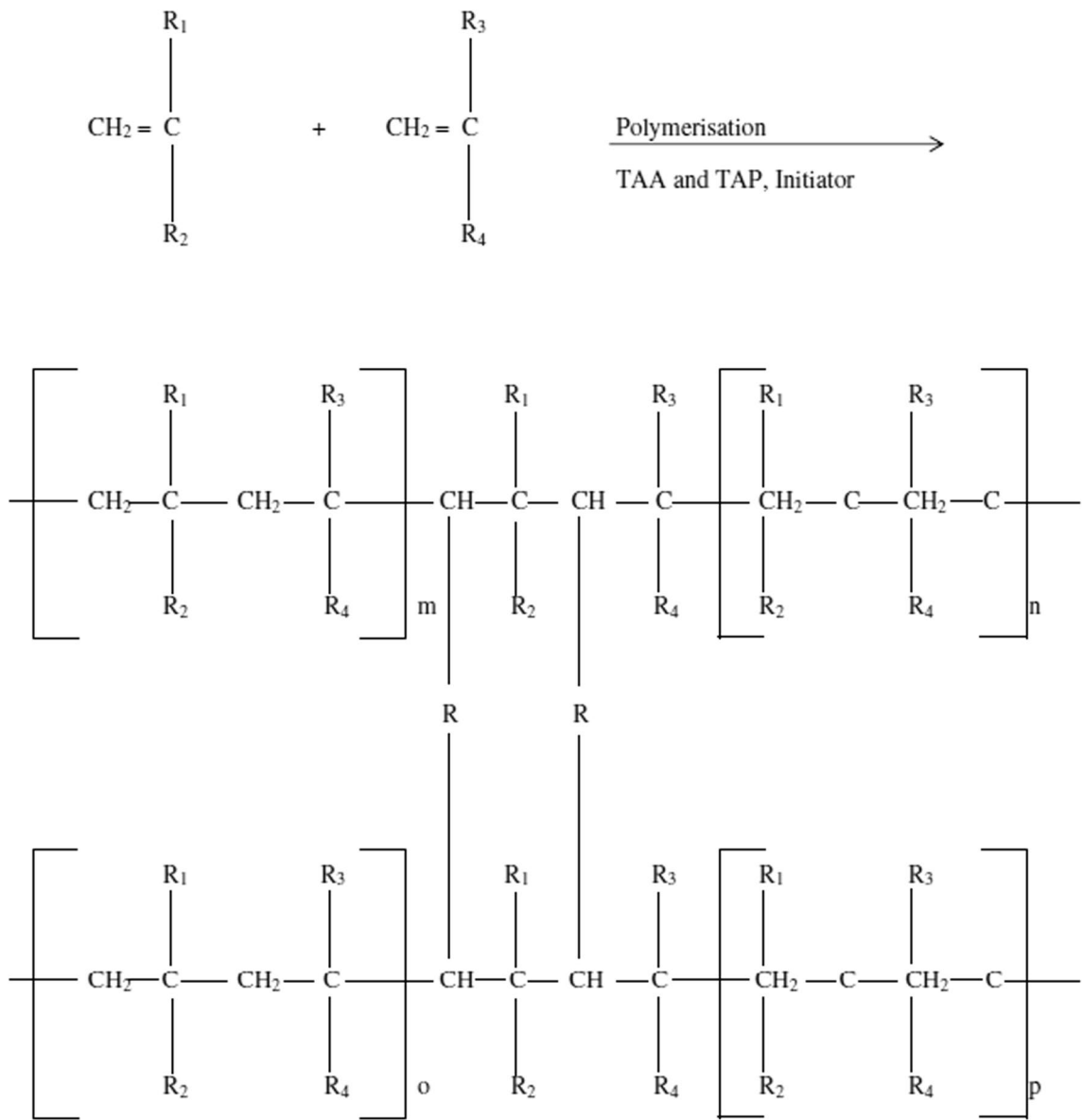


Fig. 1 General reaction scheme for SAP

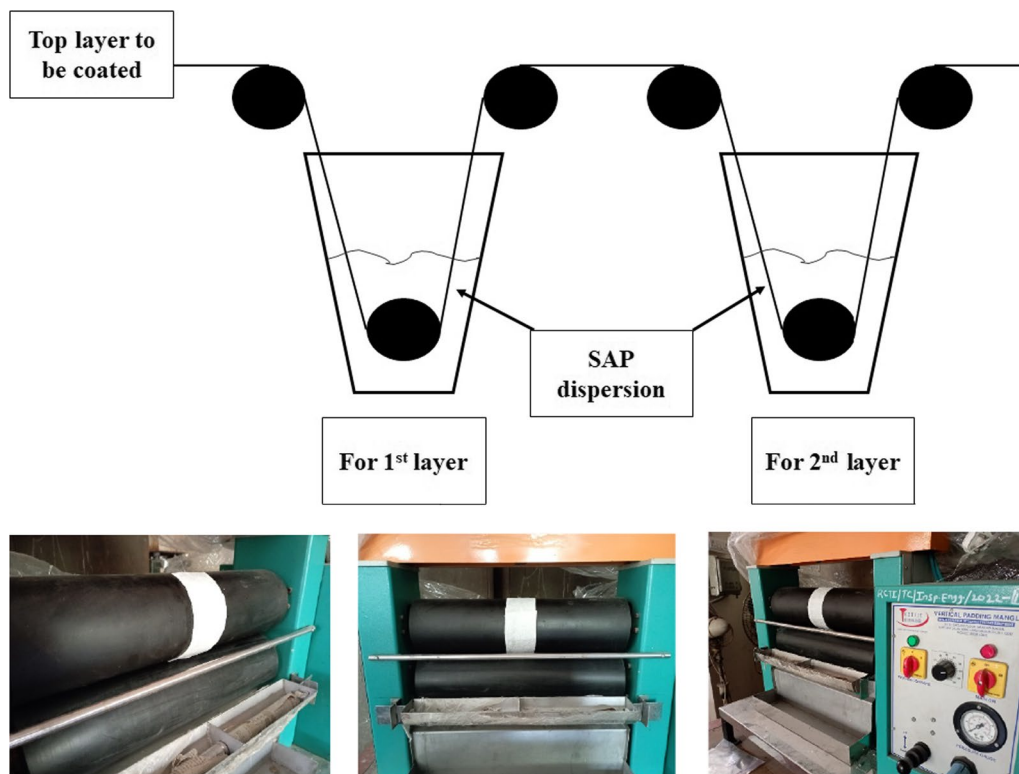


Fig. 2 Layer-by-layer application of SAP on top layer of sanitary napkin

sample weighing 0.9 g was used to completely fill the filter screen, ensuring a uniform bed. An aluminum piston was placed on the bed. The complete assembly had a weight of W_1 . Following the placement of a porous disk in a tray, tap water and saline solution were introduced. The entire assembly was positioned on the filter paper under a load of 0.3 psi, as described by Bachra et al. 2020, and EDANA 2019a. The assembly was allowed to remain unchanged for one hour. Following the designated time frame, the assembly was raised, the load was removed, and the cylinder was re-measured as W_2 . The AUL was computed using the following equation:

$$AUL \left(\frac{g}{g} \right) = \frac{(W_2 - W_1)}{W_1} \quad (2)$$

Absorbent capacity

The absorbent capacity of a superabsorbent polymer (SAP) was assessed by measuring its absorbency and absorption speed according to the EAS 96:2008-Annex C standard test procedure. Prior to adding 0.9% saline solution until saturation, the dry weight of the SAP-coated pad was recorded. Once saturation was reached, a weight of 3.4 kg was placed on the pad, as shown in Fig. 3. We used filter paper to absorb any excess fluid, and then we

recorded the weight of the pad. In this study, a saline solution was used as a substitute for blood (Mukhila and Amrutha 2023; Yadav et al. 2016). The formula presented in Eq. 3 was utilized for measurement purposes.

$$\text{Absorption Capacity}(A) = (W - X)g \quad (3)$$

where X = dry weight of the pad in gram.

W = weight of the pad underweights in gram after saturation.

Rewet back

In this test, the resistance of the SAP-coated sanitary napkin to transferring liquid that floods the coverstock to the skin is measured. Five milliliters of 0.9% saline solution was placed in the middle of a SAP-coated sanitary napkin for this test, and the solution was allowed to settle for one minute. Then, after weighing roughly 3 g in the center for 15 s, dry filter paper designated as the first was placed there. The same procedure was then carried out for the second filter paper. The study conducted tests on all the prepared samples and measured the changes between the first and second filter papers (EDANA 2018).

Strike through

A 5 ml drop of 0.9% saline solution is used to conduct the test, and the penetration time is recorded. On the



Fig. 3 Setup for measuring absorption capacity

SAP-coated napkin, a drop of test solution is allowed to fall freely, and the amount of time it takes for the solution to absorb from the top layer to the inner layer is recorded (EDANA 2018).

Determination of pH

The pH of the saline solution was determined using a pH meter. 0.5 g of the sample was slowly introduced into a 100-ml saline solution while continuously stirring. Following the solution's settling, the pH was measured (EDANA 2019b).

Antimicrobial activity

Polymer-coated samples were analyzed for antimicrobial activity against *E.coli* (gram negative) by spreading on a nutrient agar plate and incubated at 37°C for 24 to 48 h. The diameter of the inhibiting zone was measured for studying the activity against bacteria (Hassan Shibly et al. 2019). After organisms contacted the prepared samples, a % reduction was calculated for antimicrobial analysis using Eq. 4.

$$\% \text{ Reduction} = \frac{(X - Y)}{X} \times 100 \quad (4)$$

where X and Y are the cells which survived surviving cells in CFU/ml unit for the contained with prepared samples and the control one which was not coated with SAP.

Thickness of SAP-coated samples

IS 7702 test was used for analyzing the thickness of various menstrual pads (SAP-coated SAP 1–5 and commercially available CA 1–4) with the MAG-C1001 thickness tester possessing a range of 0.010–10.00 mm (Shibly et al. 2021).

Results

Characterization

Figure 4 displays the FTIR spectra of poly (MMA-co-AA). Furthermore, the figure clearly illustrates that specific selections of pH-responsive microcapsules are bolstering the selections that facilitate the coexistence of poly(MMA-co-AA). Table 3 provides the specifics of the FTIR analysis.

Absorption capacity

Table 4 shows how much superabsorbent polymer (SAP) can swell freely (FSC) and how much it can absorb under load (AUL) in tap water and saline solution. The sample with the highest FSC value, measuring 102.22 g/g, is attributed to SAP3, whereas SAP1 exhibits the lowest

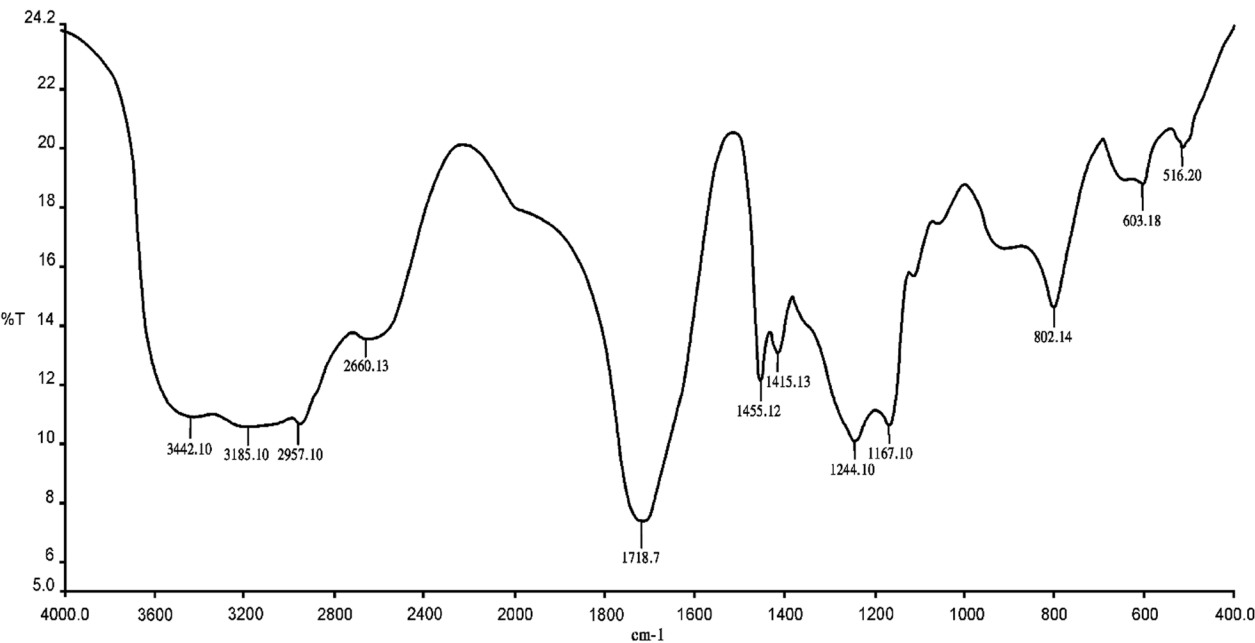


Fig. 4 FTIR of prepared SAP

Table 3 The characteristic IR bands of prepared SAP

IR band/ cm ⁻¹	Assignment(s)
3250–3600 (s, b)	Stretching of H-bonded alcoholic –OH group
2984–2960 (m, b)	C-H bond asymmetric stretching vibrations of CH ₃ group
1735–1640 (s, b)	Stretching vibration of C=O bond in acrylate carboxyl group and overlapped with bending vibration of alcoholic –OH group (confirms successful polymerization)
1449 (m)	C-H bond bending vibration of CH ₃ group
1386 (s) & 786 (w)	Stretching vibration of α-CH ₃ group (adjacent to carboxylate)
1182 (m)	In-plane-deformation of C–O–C (the polymer is present in normal plane structure which deforms)
851 (m), 959(w) and 1024(m)	Characteristic vibrational absorption bands due to >CH –CH ₂ –COOCH ₃ system
524 and 416 (w)	Vibrations of –CH ₃ group coupled with skeletal structure

Table 4 FSC and AUL

Samples	In water (g/g)	In saline solution (g/g)	
	FSC	AUL (0.3 psi)	AUL (0.3 psi)
CA1	70.2	39.28	34.25
CA2	69.5	38.22	33.81
CA3	70.8	39.89	35.21
CA4	68.2	37.25	32.18
SAP1	76.2	41.25	38.29
SAP2	83.25	43.28	40.81
SAP3	102.22	50.82	52.18
SAP4	82.5	42.79	41.23
SAP5	81.98	41.92	40.56

value. The values of SAP2, SAP4, and SAP5 are consistent with one another. The FSC value in saline water is slightly lower compared to that in tap water. The SAP3 account has a value of 52.18 g/g, whereas the remaining samples range from 38.29 to 41.23 g/g. Additionally, Table 4 shows that the AUL values are all lower than the FSC values for each sample. The range of values for tap water is 41.25 to 50.82, whereas the range for saline solution is 23.59 to 26.19. Moreover, the table presents a comparison with commercially available sanitary napkins identified as CA1, CA2, CA3, and CA4. All commercially available products have FSC values for tap water that are approximately 70 g/g, all of which are

lower than the FSC value of the prepared napkin coated with SAP. An analogous phenomenon was observed in the case of AUL. Furthermore, the SAP-coated napkins demonstrated superior value compared to commercial sanitary napkins.

Rewet back

The measurement of the wet back capacity of the sanitary napkins is done because it can prevent fluid from the napkin absorbed on the coverstock from getting to the skin. The performance analysis of samples coated with SAPs and controls is clearly displayed in Fig. 5. When compared to SAP1 and 2-coated sanitary napkins, the control sample exhibits superior wet-back characteristics. SAP3 recommends 0.1 g at the second wet test and 0.19 g at the first wet test, which are the most promising values when compared to sanitary napkins that are sold commercially and used as control samples. Wet back properties in SAP4 and SAP 5 vary slightly, and they exhibit higher values less so than in SAP3 and control. The outstanding wet back property in SAP3 is caused by the 60:40 ratio of MMA to AA, respectively. The results for the first and second wet backs for commercial products CA1, CA2,

CA3, and CA4 were also displayed. All of the values are comparable to the results of the SAP3-coated napkin, which range from 0.19 to 0.25 for the first wet back and similar values for the second wet back.

Strike through

The fluid's transit speed from the absorbent surface to the inner pad zone is determined using a strike-through test. The skin feels dry when the strike-through value is higher because it means the pad's top layer is absorbing the fluid more quickly. The fluid moves from the surface to the interior in less time 2.62 s, according to Fig. 6 because the CA3 has a faster rate of transportation. The fluid transportation in the napkin, where SAP3 was applied to the top layer, required slightly fewer seconds (2.46). The times needed to pass the fluid for CA1, CA2, and CA4 are 2.51, 2.48, and 2.46, in that order. Consequently, the amount of time needed to strike through was the same for both SAP3 and CA4. The SAP2-coated layer exhibited the longest duration, resulting in poor strike-through properties. The time for striking is drawing near in the cases of SAP1, 4, and 5.

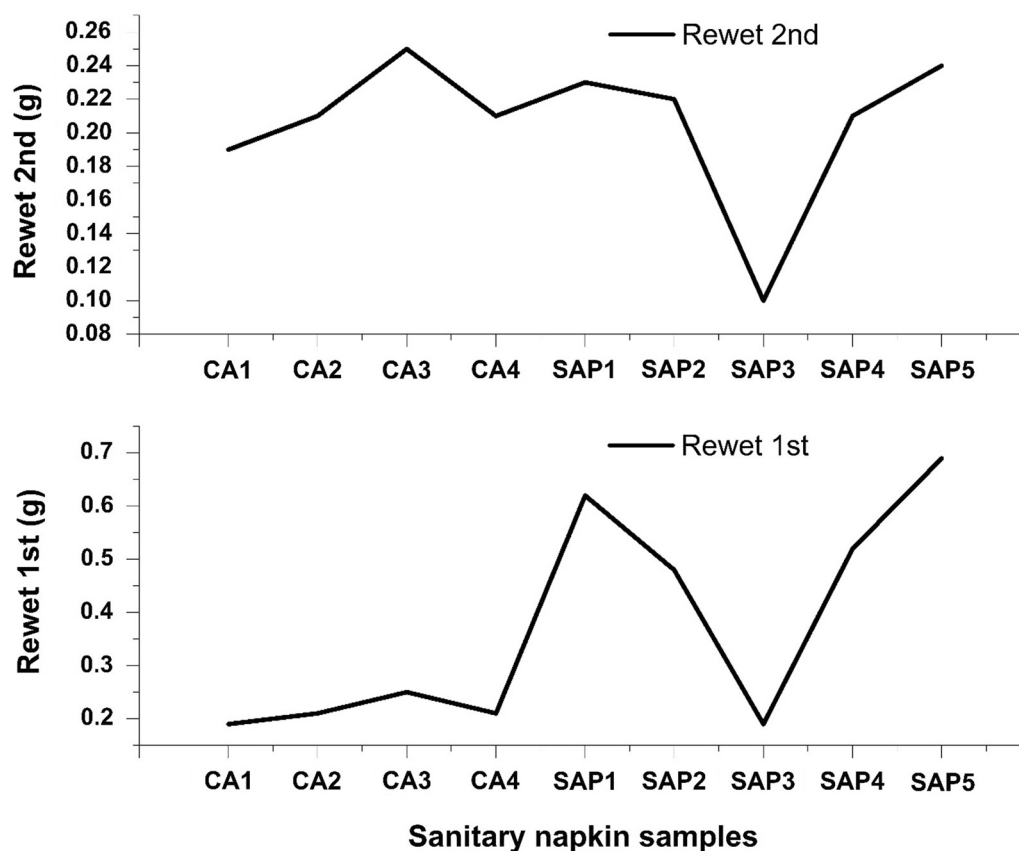


Fig. 5 Rewet (wet back) characteristics of SAP-coated napkins and commercial napkins

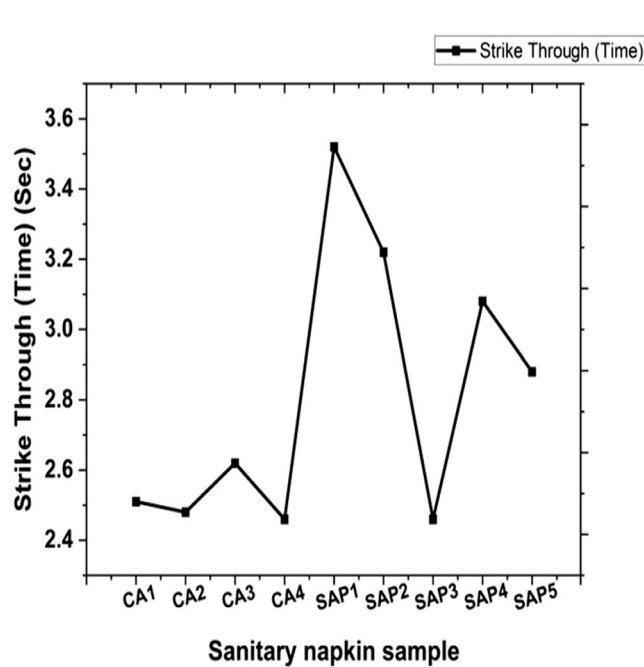


Fig. 6 Strike through of SAP-coated napkins and commercial napkins

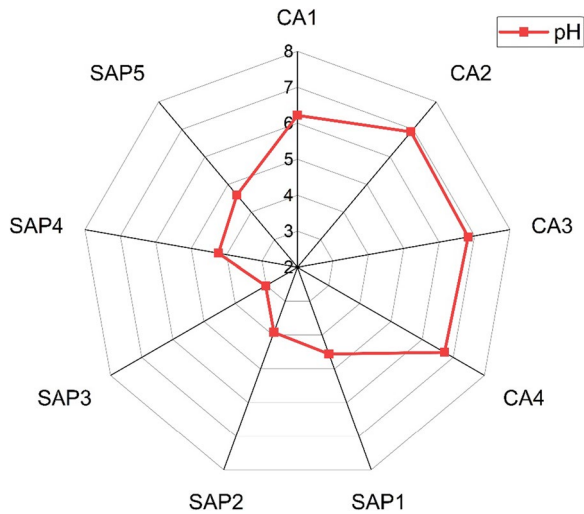
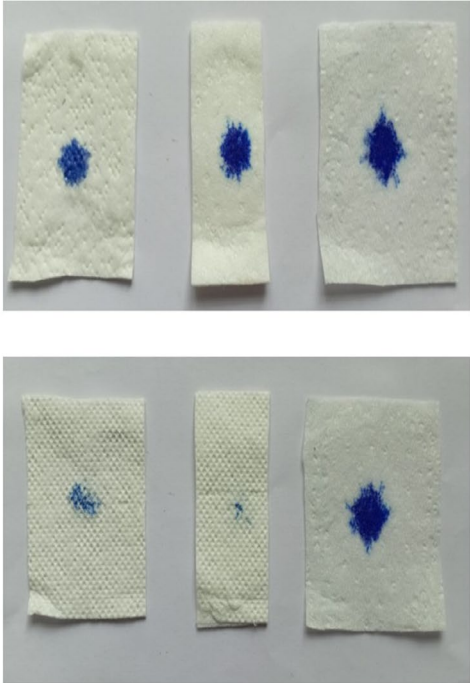


Fig. 7 pH of SAP-coated napkins and commercial napkins

pH
CA2 recommends a pH of 6.92, which is almost neutral. The prepared pad’s pH ranges from 3.02 to 4.62, with all values being acidic (Fig. 7). Since SAP3 has the lowest pH (3.02), which is more acidic, the wearer will feel more comfortable when menstrual blood with a pH of 7.4 comes into contact with the top layer of the prepared pad because of the reaction between the fluid and SAP3. It also lessens the itching. SAP1 has a pH value that is very

Table 5 Reduction of microorganisms (*E. coli*) in SAP-coated napkin, non-coated and commercially available

Samples	Survived cells against <i>E.coli</i> (CFU/ml)	Reduction (%)
Control	2.82 X 10 ⁵ (X)	
CA1	18.0 X 10 ³ (Y)	93.61
CA2	16.0 X 10 ³ (Y)	94.32
CA3	17.0 X 10 ³ (Y)	93.97
CA4	18.0 X 10 ³ (Y)	93.61
SAP1	19.0 X 10 ³ (Y)	93.26
SAP2	17.0 X 10 ³ (Y)	93.97
SAP3	14.0 X 10 ³ (Y)	95.03
SAP4	15.0 X 10 ³ (Y)	94.68
SAP5	16.0 X 10 ³ (Y)	94.32

close to the pH value of SAP3. Since SAP2, 4, and 5 have pH values above 4, they are less comfortable than napkins coated with SAP3.

Antimicrobial activity
The result shown in Table 5 clearly indicates that SAP-coated napkins suggest outstanding antimicrobial properties against *E.Coli*. The results are very comparable to the napkins available on the market, while non-coated materials are not showing any antimicrobial activity against *E.Coli*.

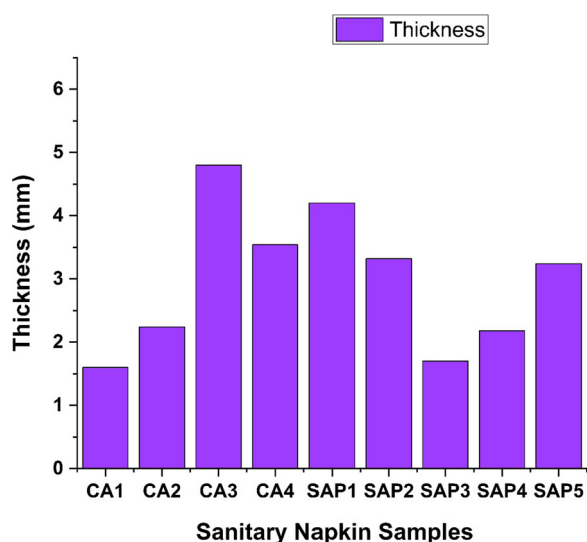


Fig. 8 Thickness of SAP-coated napkins and commercial napkins

Thickness of SAP-coated samples

As the SAP was applied to a non-woven cotton web, the thickness of the SAP-coated napkins improved, as shown in Fig. 8. CA1 shows the lowest thickness among all the samples. CA2 and CA3 have hydrophilic fiber and cotton, so thickness is higher than CA1. SAP-coated napkins

(SAP1 to SAP3) were thinner, except CA1, and the thickness of Sap1 to SAP3 was between 1.7 and 4.2 mm due to the presence of adsorbent sheets. SAP3 shows the lowest thickness value of 1.7 mm, which is near CA1.

Results and discussion

Characterization

FTIR analysis clearly supports the preparation of polymer via indicating the bands 851 (m), 959 (w), and 1024 (m). Also, 1735–1640 (s, b) denotes the presence of stretching vibration of the C–O bond in the acrylate carboxyl group and overlaps with bending vibration of the alcoholic OH group, which confirms successful polymerization. 524 and 416 (w) support the vibrations of the $-\text{CH}_3$ group coupled with skeletal structure. So, the polymer containing MMA and AA is confirmed by FTIR analysis, and the formulized copolymer is poly(MMA-co-AA).

Absorption capacity

The ability of each hygiene product to absorb water for both saline solutions and tap water is shown in Tables 6 and 7. Table 6 makes it evident that, after ten minutes, SAP3 has the maximum absorption capacity. Within a 60- to 8-h period, the weight can fluctuate between 14.84 and 132.41 g. According to the SAP3-coated feminine napkin, a 24-h maximum of 131.9 g of water can

Table 6 Water absorbency of SAPs at different time intervals

Time (s)	CA1	CA2	CA3	CA4	SAP1	SAP2	SAP3	SAP4	SAP5
10	11.06	11.6	10.69	11.28	10.3	11.64	14.84	12.7	9.5
20	13.58	14.12	13.21	13.8	12.61	13.36	20.27	18.34	11.63
30	24.19	24.73	23.82	24.41	23.25	25.46	42.04	37.06	25.69
40	47.52	48.06	47.15	47.74	47.74	49.94	71.78	70.01	51.12
50	75.65	76.19	75.28	75.87	75.82	78.85	113.84	109.2	81.1
60	93.51	94.05	93.14	93.73	94.05	97.11	132.41	129.03	102.04
480	93.51	94.05	93.14	93.73	94.05	97.11	132.41	129.03	102.04
1440	93.42	93.96	93.05	93.64	93.82	96.68	131.9	127.58	100.58

Table 7 Saline solution absorbency of SAPs at different time intervals

Time (s)	CA1	CA2	CA3	CA4	SAP1	SAP2	SAP3	SAP4	SAP5
10	14.06	14.6	13.69	14.28	13.3	14.64	17.84	15.7	12.5
20	16.58	17.12	16.21	16.8	15.61	16.36	23.27	21.34	14.63
30	27.19	27.73	26.82	27.41	26.25	28.46	45.04	40.06	28.69
40	50.52	51.06	50.15	50.74	50.74	52.94	74.78	73.01	54.12
50	78.65	79.19	78.28	78.87	78.82	81.85	116.84	112.2	84.1
60	96.51	97.05	96.14	96.73	97.05	100.11	135.41	132.03	105.04
480	96.51	97.05	96.14	96.73	97.05	100.11	135.41	132.03	105.04
1440	96.42	96.96	96.05	96.64	96.82	99.68	134.9	130.58	103.58

be absorbed. On the other hand, at intervals of 10 min, the water absorption capacities of SAP1, SAP2, SAP3, and SAP4 are 10.3, 14.84, 12.7, and 9.5 g, respectively. At the same time interval, the absorption capacities of CA1, CA2, CA3, and CA4 are suggested to be 11.06, 11.6, 10.69, and 11.28, respectively. Moreover, the absorption of all the CAs was between 93.05 and 93.96 g/g for a 24-h period. A feminine napkin coated with polymer may be able to absorb the saline solution, according to Table 7. It further supports the absorption of tap water. Over the course of 60 min to 8 h, the feminine diaper coated with SAP3 demonstrates the most efficient absorption of saline solution, with a weight of 135.41 g. During the control period, 97.05, 100.11, 132.03, and 105.04 g of saline solution were absorbed, according to the control, SAP1, SAP2, SAP3, and SAP4 samples. Likewise, the absorption values for CA1, CA2, CA3, and CA4 were 96.51, 97.05, 96.14, and 96.73 over an 8-h period, respectively.

The highest FSC values for tap water come with the use of SAP3 for coating the top layer, and other SAPs are also near each other in the numerical data. Commercially available products CA1 to CA4 also suggest FSC values close to those of other SAPs, except SAP3. Products with less fluff and more SAP that are thinner are in demand, according to the market situation. The SAP concentration of sanitary materials is limited by AUL. Although it has the potential to be raised to 50 g per gram, the hygiene industry's accepted value is currently between 18 and 30 g per gram. According to the current study, tap water has a higher absorption capacity than saline solutions. The ion content of water affects the absorption properties of SAP, which can be affected by the electrolyte in a saline solution. This is referred to as the "charge screening effect," and it occurs when the osmotic pressure difference between the SAP network and the solution decreases. It is caused by the fact that saline solutions have more NaCl cations than tap water (Fang et al., 2018; Klinpituksa & Kosaiyakanon, 2017; Likhitha et al., 2014). Therefore, electrolytes in saline solutions, which are influenced by the concentration of ions in water, can affect the absorption characteristics of SAP.

As the napkins are utilized for specific time durations, the work also analyzed the absorption capacity for certain intervals of time for each SAP-coated napkin and commercial products. The result supports SAP3, which has shown excellent absorbency (132.41 g) until 8 h, and after 24 h, the absorption decreases to 131.9 g, which is negligible. Both tables support the SAP3 for tap water and saline solution absorbency. It increases steadily for eight hours before stabilizing for twenty-four hours. At the designated interval of time, it became constant, indicating that the napkins coated with SAPs are indeed significantly absorbing the fluid with each passing moment.

Since the napkin will no longer absorb fluid after the specified amount of time, it must be changed after 8 h.

Rewet back

Wet back for first and second, due to variation in the ratio of composition of monomers used for preparing polymers, shows the variation in result, but a ratio of 64:40 (MMA:AA) has suggested the best suitability for preparing polymers, which is SAP3. Similarly, because of the cotton's hydrophilicity and SAPs' absorbency capacity, the prepared samples' top layer of needle-punched cotton and cotton also suggests that the commercial product's strike-through property is similar.

Strike through

The times needed to pass the fluid for CA1, CA2, and CA4 are 2.51, 2.48, and 2.46, in that order. Consequently, the amount of time needed to strike through was the same for both SAP3 and CA4. The SAP2-coated layer exhibited the longest duration, resulting in poor strike-through properties. The time for striking is drawing near in the cases of SAP1, 4, and 5.

pH

The pH range of the vagina is between 3.8 and 5.0, whereas the menstrual blood has a pH of almost 7.4. Because the vaginal mucosa is more acidic than blood or interstitial fluids, it can protect against pathogenic organisms (Lin et al. 2021). In order to ensure the wearer's comfort, the sanitary napkin's pH must remain acidic. Since menstrual blood will come into contact with the pad, its pH will also remain close to neutral or 7. Therefore, the pH of the sanitary napkin must be acidic at the time of menstruation, so it can manage the slightly alkaline pH of the menstrual blood and help maintain the pH of the vagina, so the wearer can feel comfort due to the itching characteristics that happen due to pH variation.

Antimicrobial activity

Improvements were found in the case of the SAP3-coated napkin, as compared with the others coated with SAP 1, 2, 4, and 5. As the molecular ratio of monomers suggests the better combination for preparing SAP, which is in the case of SAP3, bacteria decrease. As the monomer ratio changes, the antimicrobial resistance also changes.

Thickness of SAP-coated samples

The absorbance of blood determines the type of fibers in the pad; some may be hydrophilic, while others may be hydrophobic. Thickness does not necessarily exhibit high absorbency. Generally speaking, a thinner sanitary napkin indicates more even liquid distribution, which

guarantees good menstrual fluid absorption and comfort during the use of the pad.

Conclusions

To develop a feminine napkin that is both cost-effective and superior to current products, the most efficient approach is to integrate or utilize superabsorbent polymers (SAP). This will fulfil all the mentioned objectives, as there is a significant demand for such a product.

The preparation of poly (MMA-co-AA) was carried out using practical procedures, and it was subsequently applied to the upper layer of a feminine napkin. Additionally, a comparison was made between the coated product and a napkin that is readily available for purchase. Following a series of performance analyses, it was found that the cotton-carded web coated with SAP3 demonstrated the highest FSC values in both tap water and saline solutions. This suggests that the SAP3-coated cotton card is the most suitable option for feminine hygiene. SAP3 is the most suitable choice for serving tap water due to its superior AUL (absorbency under load). In addition, the top layer of feminine hygiene products is coated with SAP3, which is supported by its absorbency, reset capability, and strike-through performance. Wet back, strike-through, and pH analysis are beneficial for supporting the application of SAP 3 in coating the outer layer of sanitary napkins. The antimicrobial properties of SAP-coated napkins are more favorable as compared to commercially available products. Also, the thickness of SAP3-coated napkins is promising as it shows a negligible difference. Therefore, SAP3 is the most suitable polymer product for applying a coating to the top layer of sanitary napkins among the options available in the market.

There is a problem with the biodegradability of the prepared SAP. In order to enhance biodegradability and reduce toxicity, it is possible to produce the same polymer by grafting natural polymers. In addition, SAP can undergo surface modification, lamination, or coating with additional monomers to make it suitable for feminine hygiene applications.

Abbreviations

SAP	Superabsorbent polymer
AA	Acrylic acid
MMA	Methyl methacrylate
FTIR	Fourier transform infrared spectroscopy
BP	Benzoyl peroxide
FSC	Free swelling capacity
AUL	Absorption under load
CA	Commercially available
TBHP	Tert-butyl hydroperoxide
CFU	Colony forming unit
<i>E.coli</i>	<i>Escherichia coli</i>
MI	Millimeter

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Author contributions

CM has investigated, helped in methodologies, analyzed, and wrote draft. BP supervised, analyzed, reviewed, and rewrote draft. All authors have read and approved the manuscript.

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Preparation of microencapsulated phase change materials for use in feminine hygiene napkins based on pH response

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ABSTRACT

To create pH-responsive microcapsules, the research involved microencapsulating n-eicosane phase change material (PCM) with poly(MAA-co-ACR-co-ACN) for application on sanitary napkins. The in-situ polymerization technique was employed for polymer synthesis. SEM, FTIR, and TGA were used to verify the chemical structure and composition of pH-responsive microcapsules through morphology and core-shell structure analysis. The free swell capacity and absorption under load in tap water and saline solution were used to evaluate the absorbency of pH-responsive coated sanitary napkins. Furthermore, strike through and the pH level of every coated sample was investigated. Microcapsule coated napkins have an acidic pH value, and they are better suited for maintaining the acidic pH of the vagina during menstruation, as at the time of menstruation, pH of the blood is alkaline. So, the present work suggests the pH-responsive microcapsules for coating the top layer of feminine napkin and the comparative result suggested by SEM, FTIR, TGA, absorbency capacity, strike through and pH, clearly supports the process.

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sanitary napkin

1. Introduction

The significance of living in a world of hygiene and freshness cannot be underestimated by humans. Women's menstrual phase begins with menarche, which is a biological milestone, and an average of 1800 days in lifetime, women use the sanitary pad^[1,2] Routine menstrual period 35 ml blood has been lost generally. The situation for girls is being worsened by a lack of knowledge on menstruation preparedness and management in many developing countries. Indian society still considers menstruation to be a taboo, even though it is a natural process. The smell of menstrual fluid can be unpleasant, especially when exposed to air. The strategies of women are influenced by their personal preferences, availability of resources, economic/cultural status, and knowledge of education and menstruation^[3,4] The medical literature indicates that a large proportion of girls are not aware and unprepared for menarche or other diseases due to their inexperience with menstrual management. The environment is significantly affected by menstrual waste worldwide, India being an exception. Their daily routine involves using menstrual pads and diapers for menstrual conditions. Health is negatively affected by poor genital hygiene in either situation. When choosing sanitary pads/diapers, chemicals and microbes are also a concern. Even though

synthetic plastic materials are well known for releasing volatile organic compounds and hormone-disrupting toxins, they have been utilized as liquid absorbents to enhance efficiency^[5–7] The development of future products was focused on the thorough characterization of the fabrics used in daily sanitary pads. Polypropylene was utilized as the material for the samples in the FTIR (fourier transform infrared)/ATR (attenuated total reflectance) spectrum spectrum. Despite the Indian Government's efforts to ensure that all women are provided with sanitary pads to manage menstruation, managing menstrual waste is also a major concern. Biomaterials have been integrated into the healthcare industry to improve the quality of life for both normal and critically ill hospitalized patients, as a result of current advances. The accumulation of waste, which in turn leads to the spread of diseases, can be caused by non-biodegradable materials. The issue of neglect in managing sanitary pads, adult diapers, and similar materials is widely reported. It is imperative that we have a pad/diaper that is antimicrobial, biodegradable, and has a high holding capacity.^[8–10]

Consumption of sanitary napkins has been increased day by day, and to fulfill the demand and comfort improvement, textile industries need versatile and smart solution. So, recent scenario is concentrating

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on smart textile for anti-bacterial, water repellent, UV resistant, and such other properties related to health hygiene^[11–13] Sanitary napkin with specific properties like anti-bacterial, water absorbency in free and under load condition, have been studied and the products are available in market also. Moreover, the menstrual blood has typical odor and the pH of the same is 7.4, and the pH of vagina is generally between 3.8 to 5.0^[14] As a result, there is increment in pH wearer feel discomfort. There are many inventions and researches have been performed for super hydrophobicity by imparting hydrogel as a smart material in sanitary napkin, and they attracted consumer market also^[4,15,16] For pH controlling at the vagina pH-responsive polymer coated phase change material (PCM) can be used which may be microencapsulated. PCMs has the property of transforming from one state to another for stopping running off.^[17,18] Microcapsule is the product in which the core portion is encapsulated with hard shell for generating a very small sphere, and the process is acknowledge as microencapsulation.^[19] Physical as well chemical process can be used for microencapsulating the PCMs, and the chemical process is the mostly used and reliable as well. Various materials are studied for hard shell application and those are polystyrene, poly(methyl methacrylate), polyurethane, silica, titanium dioxide, aluminum hydroxide, zinc oxide, copper oxide, and metal oxide's hybrids also.^[17] pH-responsive polymers are those who reacts with the very small change in pH of the solution due to structural change, solubility, surface activity, and chain configuration. Commonly, pH-responsive polymers possess weak acidic or basic groups, and such groups can absorb or release hydrogen with the change in the surrounding pH.^[20,21,22]

So, in presented work, n-eicosane has been microencapsulated with poly (methacrylic acid-co-acrylamide-co-acrylonitrile) [poly(MAA-co-ACR-co-ACN)] a pH-responsive polymeric coat. n-eicosane is an organic PCM suitable for the human body by ranging with phase transition temperatures. Due to ionization of the -COOH functional group present in poly (MAA-co-ACR-co-ACN), structure is changed. This microencapsulated structure of PCM and pH-responsive polymer is used for coating the feminine hygiene napkin by showing pH-stimuli responsive controlled-release performance. As a result, pH-responsive polymer poly(MAA-co-ACR-co-ACN) helps in preventing the acidic pH during menstrual period, and PCM core material helps in maintaining the temperature at optimum level. n-eicosane was microencapsulated with pH-responsive polymer by in-situ polymerization and then coated on hygiene napkin, and the performance characteristics had been studied

for analyzing the aim of the work. The goal of this study is to open up a new zone for developing dual functional microencapsulated PCMs and applying the same on sanitary napkin for controlling the pH.

2. Material and method

2.1. Materials

Methacrylic acid (MAA), diallyl maleate (DAM), potassium persulfate ($K_2S_2O_8$) and benzoyl peroxide (BP) were obtained from A. B. Enterprise, Mumbai. n-Eicosane supplied by Shanghai Macklin Biochemical Co. Ltd. China. Acrylonitrile (ACN) and toluene were purchased from Solvochem, Ahmedabad. While acrylamide (ACR), ammonium dodecyl sulfate (ADS), nitrogen gas and liquor ammonia were obtained from Madhu Chemicals-Mumbai, Pawan Chemicals-Mumbai, Yash Organic-Mumbai, Arihant Chemicals-Vapi, Triveni Chemicals-Vapi, Sunshine Industrial Gase-Ahmedabad, Suvidhi Industry-Vapi, respectively. All the reagents used in the work are analytical grade and so used directly as received without supplementary refinement.

2.2. Preparation of pH-stimuli microcapsules

n-eicosane as a core and poly(MAA-co-ACR-co-ACN) as a shell was formulated by in-situ polymerization technique for preparing microcapsule and the route for preparing the microcapsule is shown in Figure 1. The preparation involves three stages. In the first stage, oil phase consisting MAA, DAM, and n-eicosane has been dispersed in the water by formulating the oil-in-water (O/W) emulsion with the help of ADS, an anionic detergent. In order to start the in-situ copolymerization of MAA and DAM, BP was utilized as an initiator that dissolves in oil, and the O/W emulsion was warmed to 75°C. The second stage involves the addition of MAA, ACR, and ACN co-monomers for performing copolymerization with the addition of $K_2S_2O_8$, another initiator. Finally, the shell of poly(MAA-co-ACR-co-ACN) has been developed on n-eicosane core.

The synthetic route consisting the addition of 400 ml deionized water taken in 1000 ml five neck round bottom flask (Figure 2)^[23] 18.0 g of MAA, 1.0 g DAM, 0.1 g BP, and 20.0 g n-eicosane was added in the flask by maintaining the temperature 55°C with constant stirring. 2.5 g ADS was added in above mixture after 15 minutes, and then the mixture is allowed to stand at 55°C for 2.5 hours with the purge of nitrogen. As the stable O/W emulsion is produced the temperature gradually increased to 75°C, so free radical polymerization took place under the presence of nitrogen gas, and the mixture is allowed to stand at the

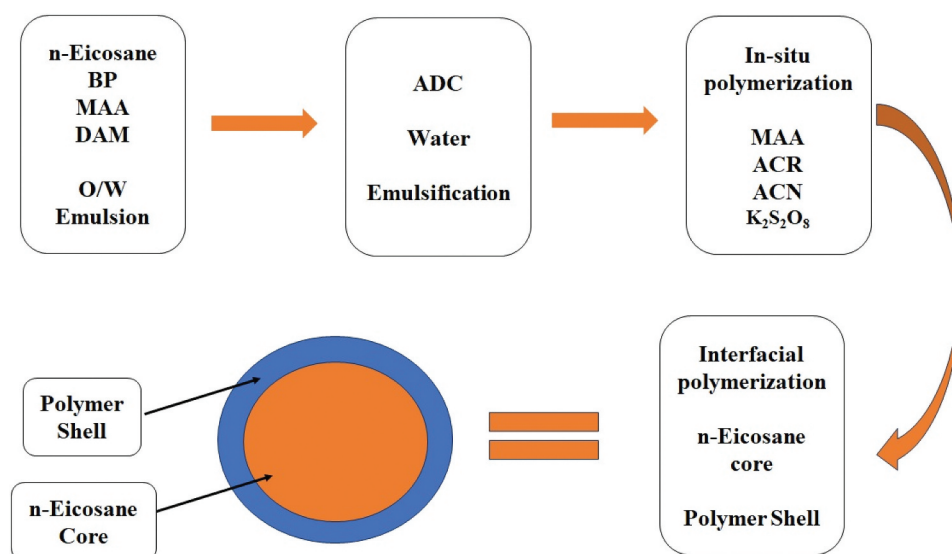


Figure 1. Synthetic route for preparing pH-responsive microcapsules.

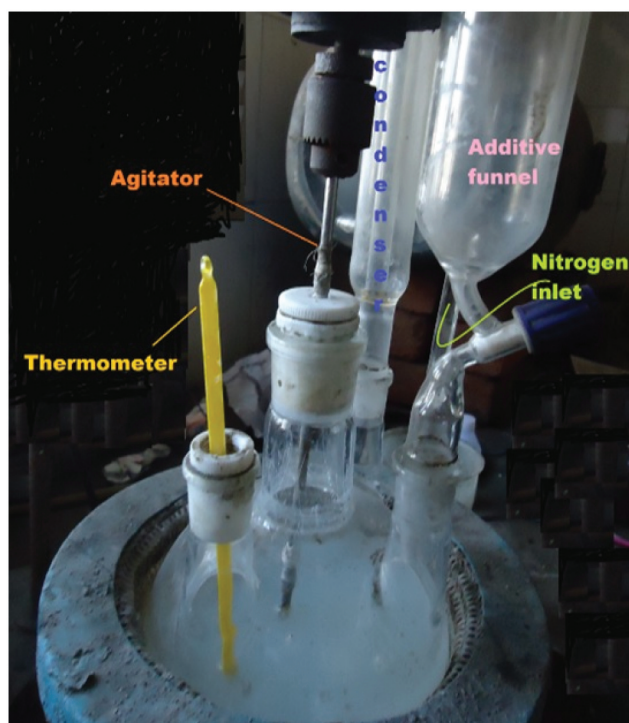


Figure 2. Assembly setup for preparing pH-responsive microcapsules.

same temperature for 3 hours with constant agitation. After 3 h, mixture of 8.0 g MAA, 4.0 g ACR, 0.2 g ACN, and 0.03 g $K_2S_2O_8$ introduced in above system. After mixing the flask was heated at 82°C for 2.5 h with constant stirring to accomplish interfacial polymerization. At the end of reaction, yield was washed with deionized water and white powders collected by filtration, which are pH-responsive polymer microcapsules. They are dried at room temperature.

2.3. Characterization

JSM 7001 F scanning electron microscope (SEM) was used for study the morphology of pH-stimuli microcapsules. Nano Measure™ software was utilized for measurement for particle size distribution and mean particle size of pH-responsive microcapsule. For FTIR (Fourier-transform infrared spectroscopy), PerkinElmer Spectrum™ 3 FT-IR spectrometer was used, which can analyze the chemical structure and composition of pH-responsive microcapsules. TGA (thermogravimetric analysis) investigations of pH-responsive microcapsules were carried out with 1.0 g of initial sample material at the heating rate of 20 K/min using Parkin Elmer TGA model 4000.

2.4. Application on Sanitary Napkin

Five layers have been formulated and fabricated for preparing the pad, including a self-adhesive tape which attached to the under garment. Tape is covered using cotton coated with paraffin wax for inhibiting leakage. Third layer is made with developed super adsorbent polymer. Again, the thin cotton has been pressed and attached to the third layer. Top layer of the pad has been made with cotton coated with formulated microencapsulated SAP.

For preparing top layer of sanitary napkin, it immersed in 30 g of pH-responsive microcapsules dispersion for 30 minutes. Then, the layer was rolled in glass rod and baked at 82°C for 3 minutes. The said process was repeated three times. Three samples were prepared: S-1 for n-eicosane, S-2 for poly(MAA-co-ACR-co-ACN) and S-3 for pH-responsive microencapsulated polymers.

2.5. Free swell capacity (FSC)

The amount of distilled water that is absorbed by the sample during its freely swollen condition is measured by this test result. In terms of convenience and speed, the tea-bag method is the best option for samples with limited quantities.^{25,26} The sample was put into a tea bag and immersed in water or saline solution for an hour after being prepared. Once the tea bag had fully swollen, it was once more weighed and its swelling capacity was calculated.

$$Fa\left(\frac{g}{g}\right) = \frac{(T_2 - T_1)}{T_1} \quad (2.1)$$

$$FSC\left(\frac{g}{g}\right) = \frac{(W_2 - (W_1 - Fa) - W_1 - W_0)}{W_0} \quad (2.2)$$

Where, T_1 and T_2 are the tea bag absorption factor, W_0 is the weight of prepared sample of sanitary napkin, W_1 is the weight of dry empty tea bag, W_2 is the weight of swollen sample.

2.6. Absorption under load (AUL)

AUL determines the capacity of SAP samples to absorb fluid at certain pressures. The filter screen was filled with an SAP sample of 0.9 grams to create an even bed. On the bed, a piston made of aluminum was placed. The entire assembly weighted W_1 . Tap water and saline solution were added after placing a porous disk in a tray (Figure 3). The whole assembly was placed on the filter paper with load (0.3 psi).^[22,24,27] The assembly was permitted to remain in its current state for an hour. After the set period, the assembly was lifted, the load was taken out, and the cylinder was reweighted as W_2 . The AUL was calculated with the following equation:

$$AUL\left(\frac{g}{g}\right) = \frac{(W_2 - W_1)}{W_1} \quad (2.3)$$

2.7. Determination of pH of top layer

pH of the saline solution was measured using pH-meter. 0.5 g of sample was added gradually to 100 ml of a saline solution with stirring. After settling of the solution, pH was measured.^[22,28,29]

2.8. Strike through

The transportation speed of fluid traveling from the surface on which it absorbs to the inner zone of pad is measured with strike through test. Higher value of strike through indicates the top layer of pad is quickly

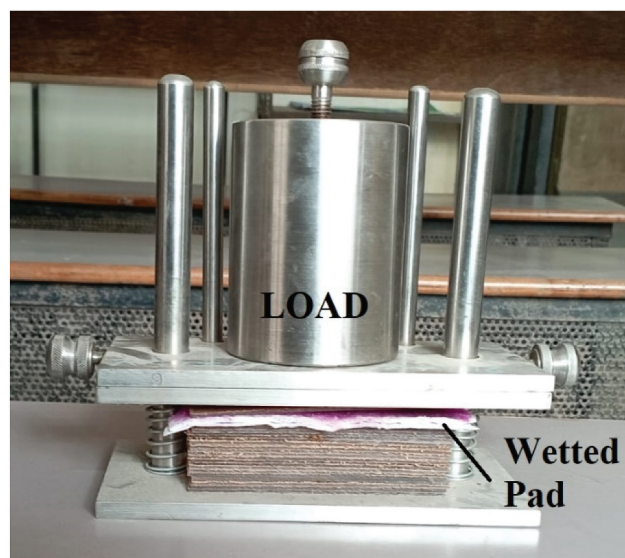


Figure 3. Assembly set up for AUL.

absorbing the fluid, and so the skin feels dry. A 5 ml drop of 0.9% saline solution is used to conduct the test, and the penetration time is recorded (Figure 4). On the microencapsulated SAP-coated napkin, a drop of test solution is allowed to fall freely, and the amount of time it takes for the solution to absorb from the top layer to the inner layer is recorded.³⁰

3. Result and discussion

3.1. Characterization

SEM analysis of pH-responsive microcapsules was performed to study the microstructure and morphology of prepared microcapsule, and the obtained result is shown in Figure 5. The figure clearly indicates that the geometry of prepared pH-responsive microcapsules is uniform and spherical in shape. Final microcapsules do not contain or shown any aggregation. Also, SEM micrographs suggests the particle size distribution of prepared microcapsule is between 1 to 20 μm , and the all-present microcapsules are showing diameter between 8 μm to 15 μm (Figure 6). SEM images in Figure 5 also support the crosslinking process, which can improve the tightness of poly(MAA-co-ACR-co-ACN) shell, as the pH-responsive microcapsules has little rough surface, and surface if crack or wrinkle free. The result of SEM give the affirmative support that the n-eicosane core has been successfully encapsulated with poly(MAA-co-ACR-co-ACN) shell by in-situ polymerization technique. FTIR of the synthesized microcapsules analyzed as suggest in Table 1. Figure 7 indicates the FTIR spectra for pure n-eicosane, poly(MAA-co-ACR-co-ACN) and microcapsules. Also from the figure, it is clear that particular

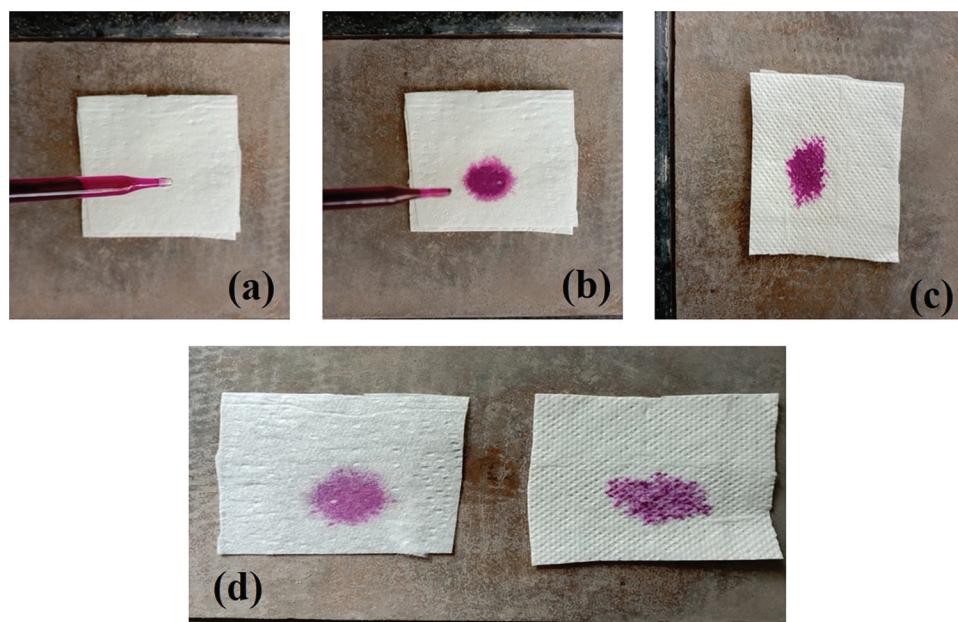


Figure 4. Strike through measurement: (a) assembly set up, (b) drop at the top layer, (c) striking through top to inner layer, and (d) top and inner layer.

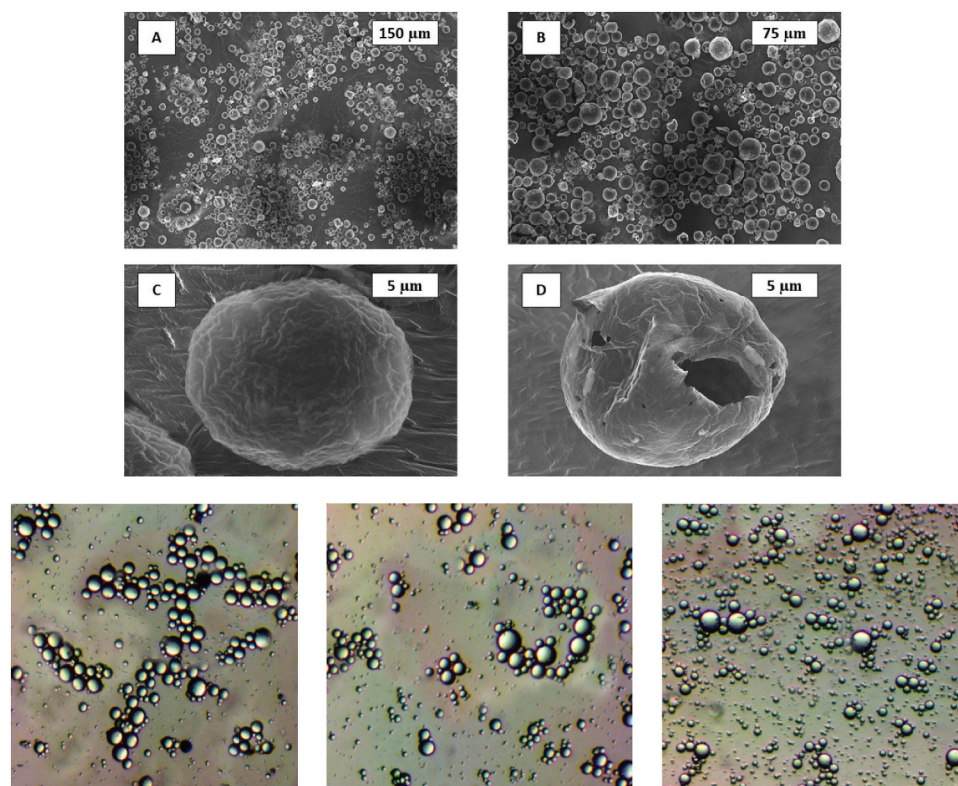


Figure 5. SEM Micrographs: (A, B) pH-responsive microcapsules, (C) close-up pH-responsive microcapsules, and (D) damaged microcapsules.

picks of pH-responsive microcapsules are supporting the picks of pure n-eicosane and poly(MAA-co-ACR-co-ACN) which support the coexistence of n-eicosane as a core and poly(MAA-co-ACR-co-ACN) as a shell.

The inspection of TGA curve ([Figure 8](#)) for pH-responsive microcapsules reveals that by heating the microcapsules a slight initial weight loss was observed due to loss of adsorbed water. The steep fall in weight

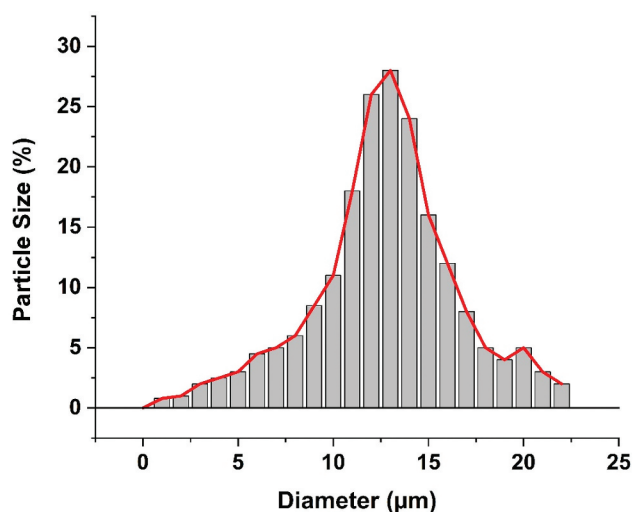


Figure 6. Particle size distribution curve of pH-responsive microcapsules.

was recorded over the temperature range of 152–247°C due to vaporization of n-eicosane. It clearly indicates the thermal degradation of poly(MAA-co-ACR-co-ACN) shell also. This second stage of significant weight loss belongs to fast degradation of poly(MAA-co-ACR-co-ACN). For microcapsules, T_{max} of n-eicosane is increases as it is capsulated with poly(MAA-co-ACR-co-ACN) shell. So, the shell of polymer decreased the thermal degradation of core by acting as a barrier.

3.2. Absorption capacity

Free swell capacity (FSC) and absorption under load (AUL) of all the samples treated with pure n-eicosane, poly(MAA-co-ACR-co-ACN) and pH-responsive microcapsules in tap water and saline solution are shown Table 2. The highest FSC value 94.23 g/g is attributed to sample prepared with S-3, While in saline water, the FSC value is comparatively lower than the value obtained with tap water. 55.87 g/g attributed to

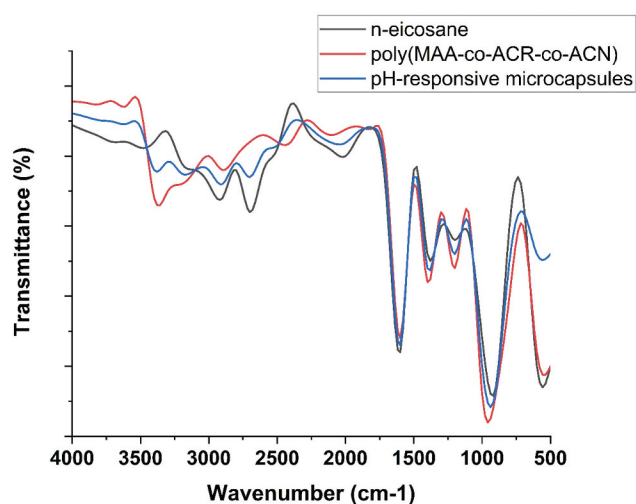


Figure 7. FTIR spectra of pure n-eicosane, poly(MAA-co-ACR-co-ACN), and pH-responsive microcapsules.

sample SAP3, while other samples are between 32.42 to 41.78 g/g.

Table 2 also suggests that values for AUL are lower than FSC for each sample. The values obtained in tap water are between 20.18 to 52, while in saline solution those are between 12.23 to 28.92. As per the market scenario, demand of the thinner hygiene with less fluff and more hydrophobicity is comparatively higher. AUL limits the amount of S-3 present in hygienic material. Currently, the value accepted by the hygiene industries is between 18 to 30 g/g, but values can be increased to 50 g/g. according to present work, in saline solution absorption capacity is decreased as compared to the tap water.^[22,27,29–31] So, the osmotic pressure is reduced between solution and hydrogel, which reduced the electrostatic force resulting in reduction of water absorption.

S-1 sample has the higher value absorption due to the presence of super absorbent polymer available in it with cotton pulp. The same phenomenon happened in the prepared S-2 and S-3 used in research work, and coated on needle punched cotton adjusted to the top layer. So, the

Table 1. The characteristic IR bands of pH-responsive microcapsules.

IR band/cm ⁻¹	Assignment(s)
350 (s)	–OH group stretching of carboxyl group
3442–3300 (s, b)	Asymmetric stretching vibration of NH ₂ group which is overlapped with alcoholic –OH group
3185 (s, b)	Symmetric stretching vibration of NH ₂ group
2957 (m, b)	C–H bond asymmetric stretching vibrations of CH ₃ group
1738 (s, b)	Characteristic stretching vibrational shoulder band of C = O bond in all poly(ACR-co-ACN) ACR was successfully copolymerized with ACN
1386–1449 (m)	C–H bond rocking vibration of CH ₃ group
1455–1415 (w)	Bending vibration of >CH– adjacent to –CO–
1244 (m)	Stretching vibrational of >CH– adjacent to –CO–
1167 (m)	In-plane-deformation of C–O–C (the polymer is present in normal plane structure which deforms)
851 (m), 959 (w), and 1024 (m)	Characteristic vibrational absorption bands due to >CH–CH ₂ –COOCH ₃ system present in PMMA
802, 603 and 516 (w)	Vibrations of –CH ₃ group coupled with skeletal structure

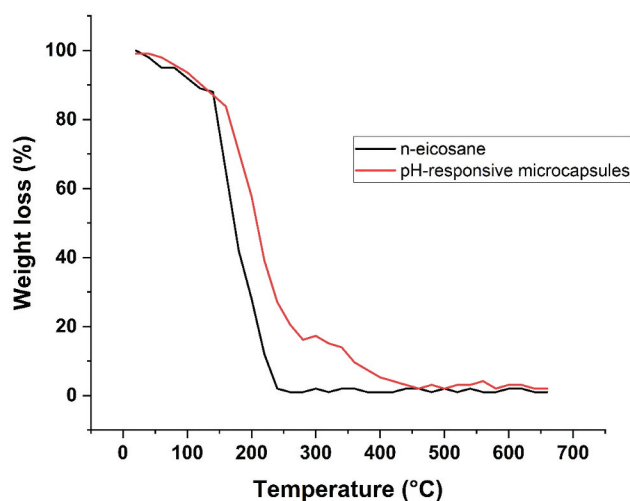


Figure 8. TGA thermograms of pure n-eicosane and pH-responsive microcapsules.

absorption of prepared napkin has also higher absorption and it can replace control one. Also, it provides necessary suppleness, liquid absorptivity, and required breathability

3.3. pH

pH of menstrual blood is nearly 7.4, while the vagina has the pH value ranges between 3.8 to 5.0. Vaginal mucosa can be protected from pathogenic organisms by having a lower pH value (more acidic) compared to blood or interstitial fluids. So, the sanitary napkin must maintain the pH at acidic level for wearer comfort. pH of each sample has been analyzed and tabulated in Table 3. S-3

Table 2. Absorption capacity of napkin.

Absorption Capacity	Samples		
	S-1 Pure n-eicosane	S-2 poly(MAA-co-ACR-co-ACN)	S-3 pH-responsive microcapsules
Free Swelling Capacity			
In water	42.25	85.64	94.23
In saline solution	32.42	41.78	55.87
Absorption Under Load (0.3 psi)			
In water	20.18	42.86	52
In saline solution	12.23	23.46	28.92

Table 3. pH of coated napkin.

pH	Samples		
	S-1 Pure n-eicosane	S-2 poly(MAA-co-ACR-co-ACN)	S-3 pH-responsive microcapsules
pH	2.94	4.26	3.08

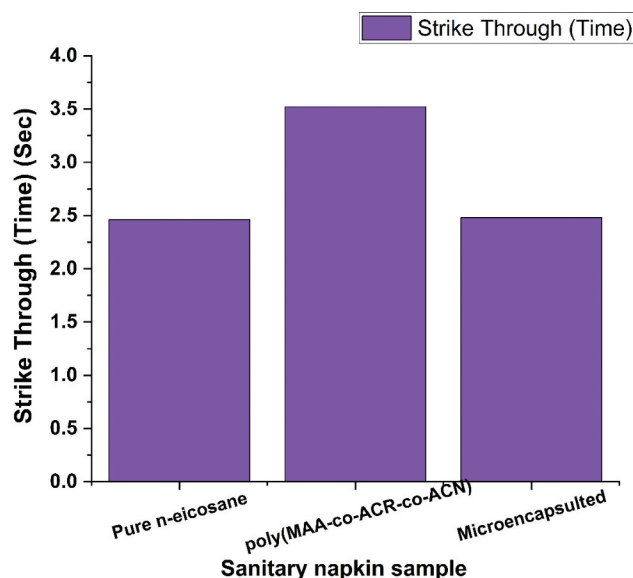


Figure 9. Strike through.

has the pH (3.02) which is acidic; so, when the menstrual blood with the pH of 7.4 will come on contact at the top layer of prepared pad, due to the reaction between fluid and S-3, the pH will lower down, and wearer will feel comfort. It also reduces the itchiness.

3.4. Strike through

Figure 9 suggests that the coated sample with microencapsulated product S-3 has the higher speed of transportation, and so, the time required for passing the fluid from surface to the inner part is less which 2.48 seconds only. Slightly lower seconds (2.46) had been required for the fluid transportation in the napkin where the top layer was coated with pure n-eicosane (S-1). Whereas, poly(MAA-co-ACR-co-ACN) S-2 coated layer has the time very near for striking. The higher strike through is received due to the presence of SAP. As the presence of cotton and needle punched cotton at top layer in prepared samples, due to hydrophilicity of cotton and absorbency capacity of SAPs, the prepared napkins also suggest the comparable strike through property with the control sample.

4. Conclusion

In the work presented here, encapsulation of n-eicosane into the poly(MAA-co-ACR-co-ACN) has been achieved successfully, which is denoted as pH-responsive microcapsules. Microcapsules contain PCM as core and pH-responsive polymer as shell. The emulsion of the microcapsules has been performed by in-situ polymerization

technique. SEM and FTIR analysis supports the formation of pH-responsive microcapsules by analyzing their chemical structure and compositions. Total absorption capacity, in terms of FSC and AUL of the cotton carded web coated with S-1 to S-3 was measured. The results have discussed in tap water and saline solution by suggesting that microcapsule coated sample shows excellent absorbency which is required by sanitary napkin. Strike through property has also shown the excellent performance in case of S-3, which is prepared during this study. Subsequently, pH measurement in saline solution performed, and the results were achieved between 2.94 to 3.08. Finally, the pH-responsible microcapsules can be utilized for coating the top layer of sanitary napkin, which controls the pH in acidic region required for vagina, and also shows the higher absorbency in free swell as well as under load.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Enhancing the efficacy of feminine hygiene sanitary napkins by developing a super absorbent polymer based on methyl methacrylate and methacrylic acid

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Abstract

Super absorbent polymer based on methyl methacrylate (MMA), methacrylic acid (MAA) has been prepared during the present work for coating the top layer of feminine sanitary napkins. Synthesized polymers were coated on the needly punched cotton and adjusted as the top layer of the sanitary napkins, which has been prepared. The samples were evaluated by means of absorbency capacity, rewet back, strike through, and pH by the comparative study with commercially available sanitary napkin. The most suitable ratio of monomers (60 g MMA, and 40 g MAA) for synthesizing polymer was suggested. Absorbency capacity of the said ratio is competing with commercial sample with 63.68 g absorbent capacity. Specially, pH of prepared polymers suggested the acidic value and those are more preferable for maintaining the acidic pH of vagina at the menstrual time. Present work suggests the polymer, which can be utilize for coating the feminine napkin by the comparative result suggested by absorbency capacity, rewet back, strike through, and pH.

KEYWORDS

feminine hygiene, polymerisation, polymers, sanitary napkins, super Absorbent polymers

1 | INTRODUCTION

Humans cannot undervalue the importance of residing in a clean and fresh environment. A woman uses a sanitary pad for 1800 days on average during her lifetime, starting the menstrual phase at menarche, a biological milestone.^{1,2} Generally, 35 mL of blood are lost during a regular menstrual cycle. The lack of awareness about menstruation readiness and management in many developing nations is making the situation worse for girls. Despite being a natural process, menstruation is still considered a taboo in Indian society. The odor of menstrual fluid can be disagreeable, particularly when it is exposed to the air. Women's strategies are shaped by their individual inclinations, access to resources, socioeconomic, and cultural standing, as well as their understanding of

education and menstruation.^{3,4} According to the medical literature, a significant number of girls lack knowledge and readiness for their first menstrual period (menarche) or other health conditions because they have not yet gained experience in managing menstruation. Menstrual waste has a substantial impact on the environment globally, with the exception of India. They use menstrual pads and diapers as part of their daily routine to manage menstrual conditions. Poor genital hygiene has a detrimental impact on health in both scenarios. When selecting sanitary pads or diapers, it is important to consider the presence of chemicals and microbes. Despite the fact that synthetic plastic materials are notorious for emitting volatile organic compounds and hormone-disrupting toxins, they have been employed as liquid absorbents to improve effectiveness.^{5–7} The development of future

products was centered on the comprehensive characterization of the textiles utilized in everyday sanitary pads.

Although the Indian Government strives to ensure that all women have access to sanitary pads for menstrual management, the proper disposal of menstrual waste remains a significant issue. Current advancements have led to the integration of biomaterials into the healthcare industry, aiming to enhance the quality of life for both hospitalized patients who are critically ill and those who are not. Nonbiodegradable materials can cause the accumulation of waste, which in turn can lead to the spread of diseases. The problem of negligence in the management of sanitary pads, adult diapers, and similar materials is extensively documented. We require a pad/diaper that possesses antimicrobial properties, is biodegradable, and has a substantial holding capacity.^{8–10} Making a sanitary pad that is antimicrobial, biodegradable, and has good water absorption capacity is the aim of this research. It can serve as a diaper or as a menstrual pad for both children and adults.

2 | MATERIALS AND METHODS

2.1 | Materials

All the chemicals were of laboratory grade and utilized after their purification. Solvents used in experimental work were distilled before their use. Methyl methacrylate (MMA), methacrylic acid (MAA), diallyl maleate, and benzoyl peroxide (BP) were obtained from A. B. Enterprise, Mumbai. Triallylamine and triallylphosphite were imported from Shandong Luyue Chemical, China. Diallylphthalate, ethyl Acetate (EA), tert-butylhydroperoxide (TBHP), nitrogen gas, and liquor ammonia were obtained from Madhu Chemicals-Mumbai, Pawan Chemicals-Mumbai, Yash Organic-Mumbai, Arihant Chemicals-Vapi, Triveni Chemicals-Vapi, Sunshine Industrial Gase-Ahmedabad, and Suvidhi Industry-Vapi, respectively.

2.2 | Synthesis of super adsorbent polymer

Integrated with a five-necked round bottom flask with a capacity of 1000 mL is an impeller agitator with dual helices, a thermometer, an additive funnel, an inlet for nitrogen gas, and a vacuum condenser. The flask was filled with 200 mL of a 60:40 solvent mixture comprised of 120 mL toluene and 80 mL EA and two small porcelain chips were added. Heat the solvent mixture slowly to 40°C and then use nitrogen gas to sparge the contents of the flask, removing the air. The additive funnel is filled with 50 mL of monomer feed (containing solvent mixture, monomers, and cross linker) and the feed is added drop wise at the rate of 3.0 mL/min under a continuous stream of nitrogen gas. To initiate polymerization, BP is added at the same time and the temperature is gradually elevated to 80°C. When addition of 50 mL monomer feed is completed, the remaining 200 mL of the monomer feed is transferred into the additive funnel and it is added drop wise over a period of 1.5 h. Temperature remains within 80–90°C throughout the polymerization process. The polymerization reaction is inhibited by adding 0.01 percent by weight of TBHP at the end of the reaction. To remove solvents, the polymer product is distilled in a rotary evaporator under vacuum after the polymerization process is complete. The same procedure is performed for the series with different composition of monomers as shown in Table 1. The amount of polymer product that is produced is almost quantitative.

2.3 | Pad preparation

Five layers have been formulated and fabricated for preparing the pad, including a self-adhesive tape, which attached to the under garment. Tape is covered using cotton coated with paraffin wax for inhibiting leakage. Third layer is made with developed super adsorbent polymer. Again, the thin cotton has been pressed and attached to the third layer. Top layer of the pad has been made with

TABLE 1 Components and amounts are set forth for polymers super adsorbent polymer (SAP) A–SAP E.

Sample notation	MMA (g)	MAA (g)	Triallylamine and triallylphosphite (g)	Toluene (ml)	Ethyl acetate (ml)	Temperature (°C)
SAP A	80	20	0.01	240	160	80–90
SAP B	70	30	0.01	240	160	80–90
SAP C	60	40	0.01	240	160	80–90
SAP D	50	50	0.01	240	160	80–90
SAP E	40	60	0.01	240	160	80–90

Abbreviations: MAA, methacrylic acid; MMA, methyl methacrylate.

cotton coated with formulated super adsorbent polymer (SAP) (Figure 1).

2.4 | Absorbent capacity

To evaluate the absorbency and absorption speed of an SAP, absorbent capacity has been measured using EAS 96:2008-annex C standard test procedure. A dry weight of the SAP coated pad noted first, and then till saturation 0.9% saline solution has been added. After achieving saturation 3.4 kg weight was loaded on the pad (Figure 2). Filter paper was utilized for soaking of excess fluid, and the weight of pad noted. Here, saline solution was taken in place of blood.^{11,12} For measuring formula shown in Equation (1) was used.

$$\text{Absorption Capacity } (A) = (W - X)g, \quad (1)$$

where, X = dry weight of the pad in gram and W = weight of the pad underweights in gram after saturation.

2.5 | Rewet back

This test measures the resistance of the SAP-coated sanitary napkin in transferring fluids from the cover stock to the skin. During the test, 5 mL of 0.9% saline solution was applied to the center of a SAP-coated sanitary napkin, and allowed to settle for 1 min. Weighing approximately 3 g, a dry filter paper was placed at the center for 15 s, first for one filter paper and then repeated for another filter paper. All samples were tested, and the difference between the first and second filter paper was measured.¹³

2.6 | Strike through

The test involves applying a 5 mL drop of 0.9% saline solution and measuring the penetration time. A drop of test solution is released onto the SAP-coated napkin (Figure 3), and the time taken for the solution to be absorbed from the top layer to the inner layer is monitored.¹³

2.7 | pH of SAP layer (top layer)

A pH meter was utilized to assess the acidity level of the top layer of a sanitary napkin coated with prepared SAP, which is in close proximity to the skin. The equipment was calibrated using buffer solutions with pH values of

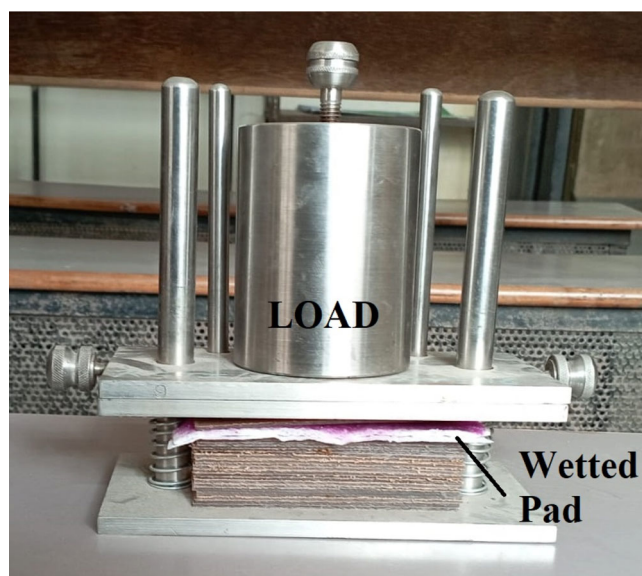


FIGURE 2 Absorbent capacity measurement assembly with load. [Color figure can be viewed at wileyonlinelibrary.com]

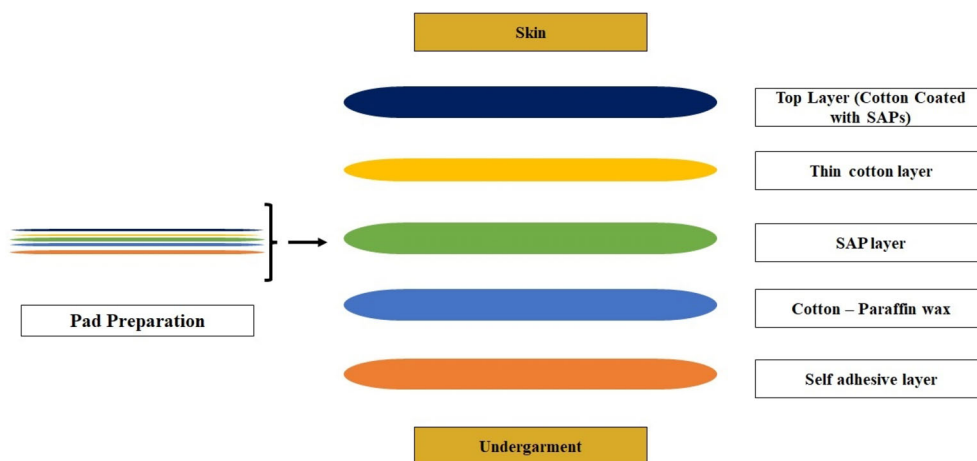


FIGURE 1 Pad preparation with layers. [Color figure can be viewed at wileyonlinelibrary.com]

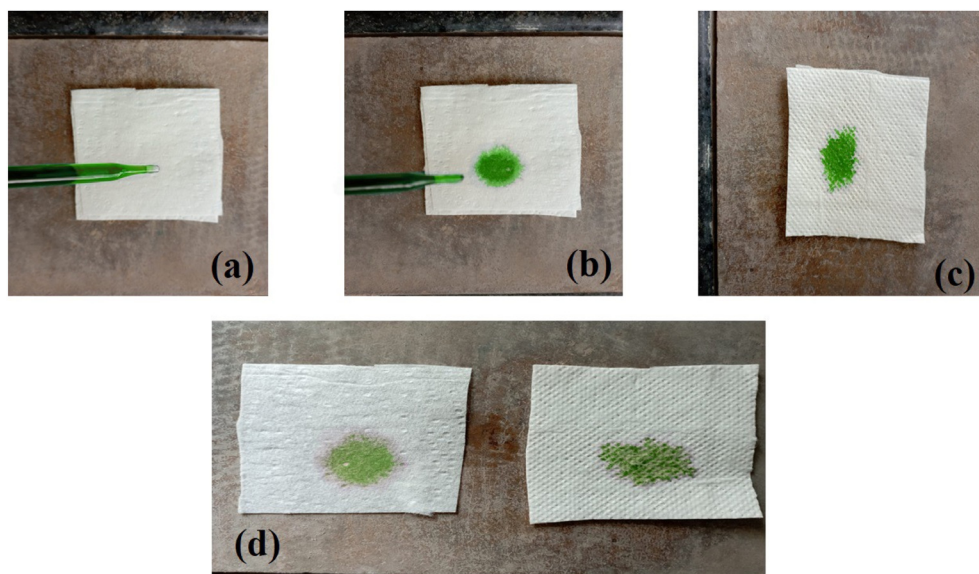


FIGURE 3 Strike through measurement (a) assembly set up, (b) drop at the top layer, (c) striking through top to inner layer, and (d) top and inner layer. [Color figure can be viewed at wileyonlinelibrary.com]

4 and 7 (Figure 4). A total of 100 mL of distilled water was placed in a 250 mL flask, and 1 g of sample, diced into little pieces, was added to it. The components were placed on a rotary shaker and mixed for 20 min. The pH of each filtered extract was finally measured.¹⁴

3 | RESULT AND DISCUSSION

3.1 | Polymerization

A proposed general reaction scheme for polymers SAPA-E, is presented in Figure 5. The various pendant groups R_1 , R_2 , R_3 , and R_4 are defined in Table 2.

3.2 | Absorbent capacity

Absorption capacity of prepared napkin with SAPs coated cotton at top layer has been measured against the control napkin, which is available in market. Control sample indicates the absorption of 63.6 g of saline solution. SAP-C at top layer in napkin shows exactly 63.68 g absorption, which is very close to the result of sanitary pad available in market (Figure 6). SAP-E, B, and D have the lower value compare with SAP-C coated sanitary napkin and those are 60.28, 61.34, and 62.24 in incremental order, respectively. SAP-A has lower absorption of saline solution compare with other SAPs and control samples. Control sample has the higher value absorption due to the presence of SAP available in it with cotton pulp. The same phenomenon happened in the prepared acrylate-based polymer used in research work, and coated on needle punched cotton adjusted to the top layer. So, the absorption of prepared SAPs coated napkin has also



FIGURE 4 pH meter. [Color figure can be viewed at wileyonlinelibrary.com]

higher absorption and it can replace control one. Also, it provides necessary suppleness, liquid absorptivity (Figure 7), and required breathability.

3.3 | Rewet back

The test is performed to measure the wet back capacity of the sanitary napkin, which can hinder the transportation of fluid to the skin from napkin absorbed on cover stock. Figure 8 clearly indicates the performance analysis of control and SAPs coated samples. Control sample has the excellent wet back properties compare to SAP-A, and B coated sanitary napkin. While SAP-C suggests 0.3 g at first wet and 0.1 g at second wet test, which are the most promising values compare to commercially available

FIGURE 5 Proposed reaction mechanism for polymerization of super adsorbent polymer A–E.

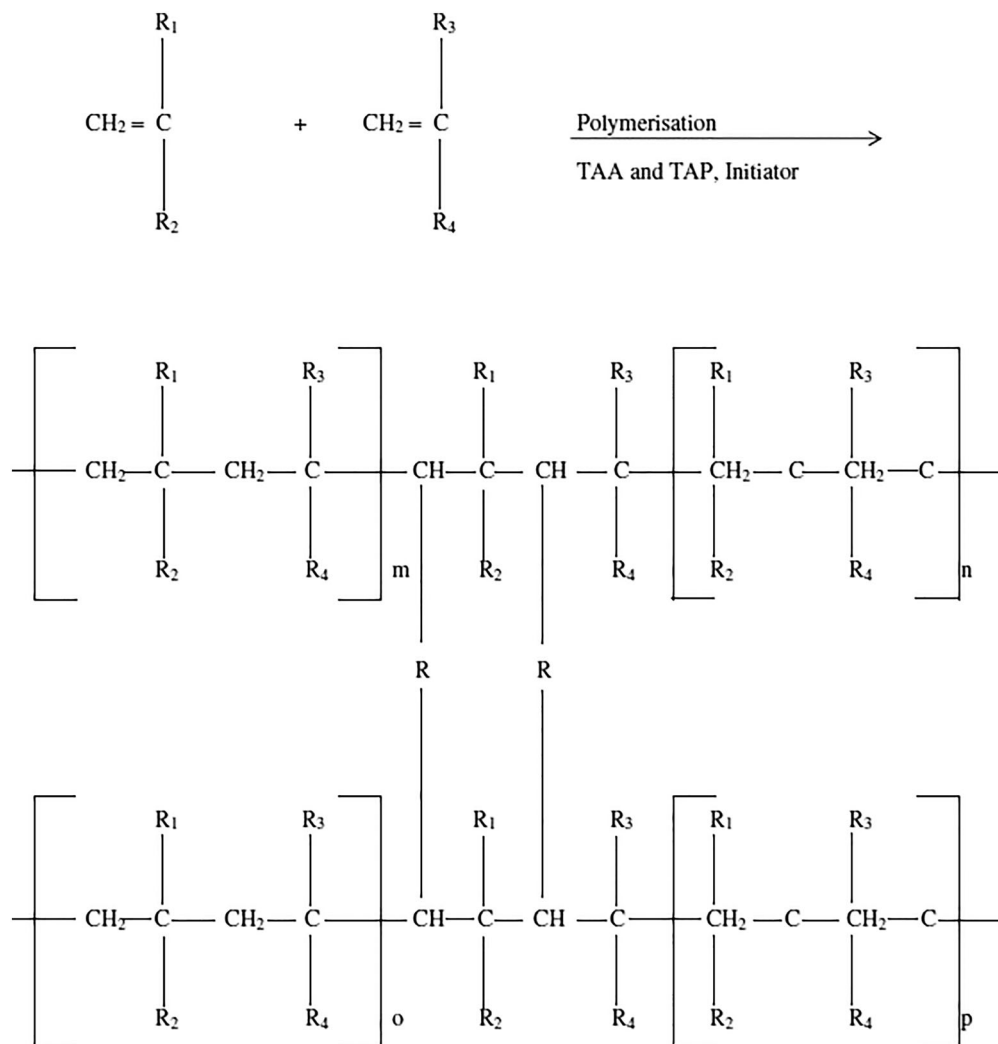


TABLE 2 Components of monomers in reaction scheme suggested in Figure 1.

Polymers	Monomers	R ₁	R ₂	R ₃	R ₄
SAP A–E	MMA and MAA	CH ₃	COOCH ₃	CH ₃	COOH

Abbreviations: MAA, methacrylic acid; MMA, methyl methacrylate; SAP, super adsorbent polymer.

sanitary napkin taken as control samples. SAP-D and E have slight variation in the wet back properties, and those are showing higher value in less manner to the SAP-C and control. 60:40 ratio of MMA and MAA, respectively, is the responsible for excellent wet back property in SAP-C. For other SAPs, they are showing variation in the wet back result due to the variation in the ration of their composition used for preparing polymers.

3.4 | Strike through

The rate at which fluid moves from the surface where it is absorbed to the inner part of the pad is determined using the strike-through test. A higher strike-through number indicates that the top layer of the pad is rapidly

absorbing the fluid, resulting in the skin feeling dry. Figure 9 indicates that the control sample has a faster transportation speed, resulting in a shorter time of 2.48 s for the fluid to flow from the surface to the inner section. The fluid transit in the napkin with the top layer coated with SAP-C took slightly less time, specifically 2.46 s. The SAP-B coated layer took the longest time, resulting in poor strike-through properties. SAP, A, D, and E are close to taking action imminently. The increased strike through is caused by the presence of SAP in both commercial and prepared pads. The presence of cotton and needle-punched cotton in the top layer of the prepared samples, along with the hydrophilicity of cotton and absorbency capacity of SAPs, indicates that the prepared napkins also exhibit a comparable strike-through property to the control sample.

3.5 | pH

pH of menstrual blood is nearly 7.4, while the vagina has the pH value ranges between 3.8 and 5.0. Vaginal mucosa can be protected from pathogenic organisms by having a lower pH value (more acidic) compared with blood or interstitial fluids.¹⁵ So, the sanitary napkin must maintain the pH at acidic level for wearer comfort. Control sample suggested the pH of 6.89, which is nearly neutral, and as the menstrual blood will come in contact with the pad, it will also remain near neutral pH, that is, 7. pH of

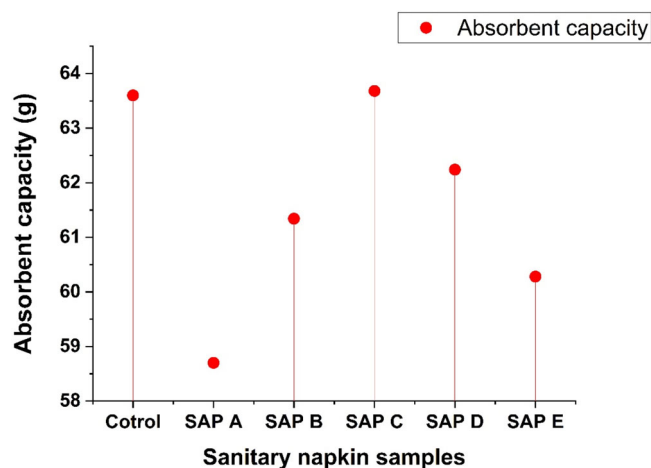


FIGURE 6 Absorbent capacity of super adsorbent polymers (SAPs) coated napkin. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 Super adsorbent polymer after absorption. [Color figure can be viewed at wileyonlinelibrary.com]

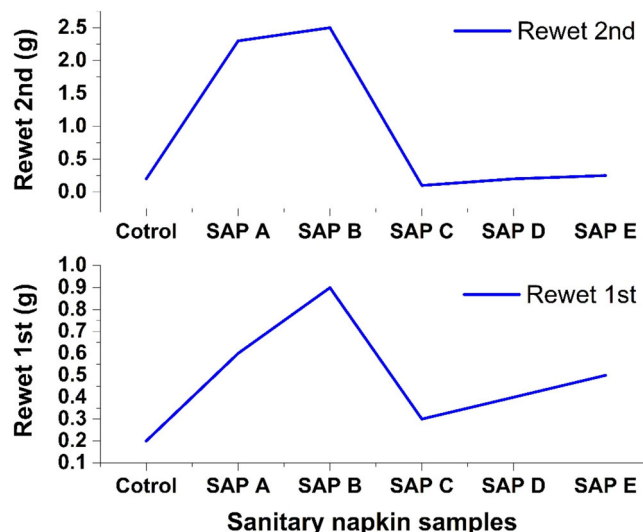


FIGURE 8 Rewet back of super adsorbent polymers (SAPs) coated napkin. [Color figure can be viewed at wileyonlinelibrary.com]

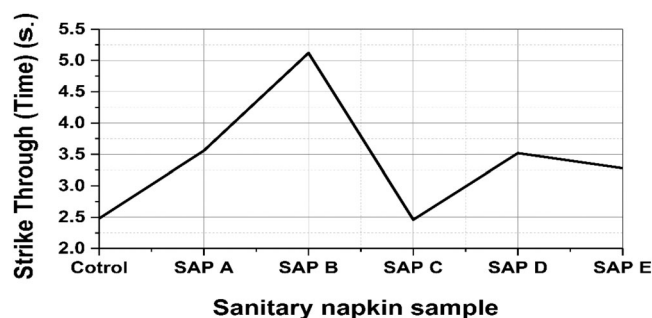


FIGURE 9 Strike through of super adsorbent polymers (SAPs) coated napkin.

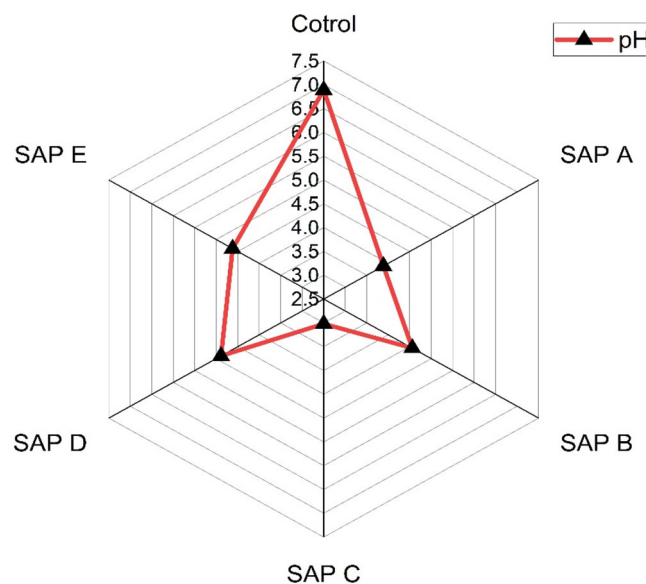


FIGURE 10 pH of super adsorbent polymers (SAPs) coated napkin. [Color figure can be viewed at wileyonlinelibrary.com]

prepared pad is varying between 3.02 and 4.89, and all are acidic (Figure 10). SAP-C has the lowest pH (3.02), which is more acidic, so when the menstrual blood with the pH of 7.4 will come on contact at the top layer of prepared pad, due to the reaction between fluid and SAP-C, the pH will lower down, and wearer will feel comfort. It also reduces the itchiness. SAP-A has also very near to the SAP-C pH value. SAP-B, E, and D are above 4 pH, and therefore they have lower comfortability compare to SAP-C coated napkin.

4 | CONCLUSION

Absorbency capacity of the SAP-C coated napkin prepared in this study has the similar value indicated by commercially available napkin. Similarly, SAP-C has suggested exactly or very close value in rewet, strike through properties with the control sample. Specifically, in the case of pH SAP-C has the pH very lower, that is, acidic compare to control one, as the control show 6.89 pH near neutral. Lower pH has the benefit of maintaining the acidic pH near the region of vagina, which must be acidic naturally (3.8–5.0). Control sample has the neutral pH, and so when fluid comes in contact with the same, it will remain neutral as the fluid has the pH value of 7.4. Hence, the SAP-C with the pH value 3.02 is the best suitable for coating at the top layer, which can immediately reduce the pH of fluid and increase the comfort level. Overall, the study supports the SAP-C coated top layer pad prepared during whole work is the best suitable compare to others polymer prepared and also commercially available sanitary napkin, especially in the case of pH maintenance.

AUTHOR CONTRIBUTIONS

Chintan Madhu: Conceptualization (lead); formal analysis (equal); investigation (equal); methodology (lead); resources (equal); writing – original draft (lead). **Bharat Patel:** Investigation (supporting); methodology (supporting); resources (supporting); supervision (lead); validation (lead); writing – review and editing (lead).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available at DOI: [10.1016/j.srhc.2015.06.001](https://doi.org/10.1016/j.srhc.2015.06.001). <https://pubmed.ncbi.nlm.nih.gov/26614609/>

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RESEARCH ARTICLE



Formulation and characterization of super absorbent copolymer AA, ACN-grafted sodium acrylate for feminine napkin

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ABSTRACT

Absorbency for feminine napkins is a research priority in the recent era, though commercial napkins are available with the same function properties achieved through finishing. One of those methods is coating SAPs, which act as hydrogels. Super absorbent polymers are generally coated in the second- or third-layer of the napkin. The present work deals with the coating of the SAP on the top layer by forming poly (acrylic acid)/sodium acrylate (ACN-g-PAA/SA) and demonstrating its absorption properties. Ultimately, we conducted a comparative analysis of all the SAPs prepared, and demonstrated an absorptive capacity of 104.35 g/g in tap water and 51.28 g/g in saline solution during free swelling. Additionally, under a specific load, it demonstrated 56.48 g/g in tap water and 27.42 g/g in saline solution. Based on the comparative results suggested by the TGA curve, water absorbency, and moisture content, the present work proposes a polymer suitable for coating the feminine napkin.

ARTICLE HISTORY

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KEYWORDS

Acrylonitrile; sodium acrylate; super absorbent; water absorbency; feminine hygiene

1. Introduction

The feminine hygiene market dominates everywhere, which includes tampons, sanitary napkins, menstrual cups, and vaginal health products. The 2022-feminine hygiene market survey indicated that the global value of the feminine hygiene market would reach 42 billion dollars by 2022, up from 35.4 billion U.S. dollars in 2016. Each woman consumes approximately 60 kg of feminine napkins per year, which generates 10 crores of kg of waste. We can achieve higher absorbency in these sanitary napkins by adding a super absorbent polymer to their structure. Chemically, super absorbent polymer (SAP) materials have hydrophilic crosslinked networks that can take in a lot of water or aqueous solutions and hold them even when they are under pressure. It is important to note that the polymer's absorbent capacity is not the same as its dry weight (Francis et al., 2004). SAPs have unique qualities, and they are useful for their application in hygienic products, particularly disposable diapers (Kosemund et al., 2009) and napkins (Liu et al., 2014). The partially neutralized and lightly crosslinked polymers in SAPs typically form three-dimensional polymer networks that expand upon water absorption. It is important to consider their absorbing capacity, liquid uptake rate, mechanical gel strength, and liquid retention. Most current super absorbents, made using solution or inverse-suspension polymerization methods, contain acrylic acid (AA), its salts, and acrylamide (AM) as main ingredients. Synthetic polymer-based soaps are capable of absorbing water, but their toxicity and non-biodegradability can lead to environmental problems. Therefore, more attention has been given to SAPs based on natural polymers in

recent trends. Biodegradable polymers commonly synthesize using carbohydrate polymers such as cellulose, starch, chitin, alginate, and other types of carbohydrates (Parvathy & Jyothi, 2012). Guilherme et al. (2015) analyze superabsorbent hydrogels, biodegradable polymers, for their application in agriculture. Also, the biodegradable SAPs were synthesized by grafting acrylamide onto starches and then cross-linking them with N-methylene-bisacrylamide for application in agriculture (Zou et al., 2012). The same purpose was studied for the starch-graft-acrylamide/mineral powder superabsorbent composite to analyze its synthesis and properties (Wu et al., 2003). Polymerization of starch and AA by graft polymerization was performed to synthesize superabsorbent in the presence of attapulgit micropowder in an aqueous medium (Li et al., 2007). Chitin is a crucial natural polymer, and chitosan is a form that has been highly N-deacetylated for preparing SAPs. Chemical reactions can modify their chains due to the presence of many hydroxyl and amino groups. The CMCTS-g-PAA absorbent polymer was created by grafting acrylic acid onto carboxymethyl chitosan and then crosslinking it (Chen & Tan, 2006). The super-absorbent hydrogel was created by grafting sodium acrylate and 1-vinyl-2-pyrrolidone to the chitosan chain. The prepared SAP has a high absorption rate, and the swelling process of the polymer fitted the first-order kinetics; also, its swelling ratio was dependent on the pH (Chen et al., 2009). Poly (vinyl alcohol) and chitosan were synthesized through UV irradiation, and their swelling behaviors were investigated (Kim et al., 2003). Another important natural polymer is cellulose. A superabsorbent polymer based on carboxymethyl cellulose (CMC) and polyvinylpyrrolidone (PVP) was prepared using gamma irradiation as a clean and environmentally friendly

source of initiation and crosslinking (Raafat et al., 2012). The study of NaCMC-g-PAA synthesized by grafting acrylic acid onto sodium carboxymethyl cellulose through inverse suspension polymerization (Klinpituksa & Kosaiyakanon, 2017).

The strategy of incorporation of microsized or nanosized materials in superabsorbent hydrogel (SH) formulations based on cellulose and chitin to obtain desired properties was investigated (Rodrigues et al., 2014). Many studies have also been done on tragacanth in the different fields of drug delivery systems, such as the removal of heavy metal ions (Hemmati & Ghaemy, 2016; Masoumi & Ghaemy, 2014; Sahraei & Ghaemy, 2017), superabsorbents (Khoylou & Naimian, 2009), and so on. In this study, we have synthesized a novel superabsorbent based on acrylic acid, acrylonitrile, by grafting the reaction of the bath onto sodium acrylate in an aqueous medium. Furthermore, we investigate the suitability of the superabsorbent at various pHs for its application in hygiene textiles.

2. Experimental

2.1. Materials

A.B. Enterprise (India) provided acrylic acid (AA) (CAS Number: 79-10-7) and acrylonitrile (ACN) (CAS Number: 107-13-1) to clean after a 10% solution of sodium hydroxide (CAS Number: 1310-73-2) was used and deionized water was used for washing. We collected Methylene bisacrylamide (MBA) (CAS Number: 110-26-9), potassium persulfate (KPS) (CAS Number: 7727-21-1) from A.B. Enterprise, and sodium acrylate (SA) (CAS Number: 7446-81-3) from Dev International through a trusted manufacturer.

2.2. Preparation of acrylonitrile-g-poly(acrylic acid)/sodium acrylate (ACN-g-PAA/SA) superabsorbent

The procedure followed to synthesize a series of superabsorbents from ACN, AA, and SA. Appropriate amount of ACN was dissolved in 30 ml of ml of acetic acid solution (1%) in a 250 ml five-neck flask equipped with a mechanical stirrer, a reflux condenser, a funnel, a nitrogen line, and a thermometer a thermometer (Figure 1). We used nitrogen for 30 min to remove the dissolved oxygen from the system, and then added KPS to initiate ACN and generate radicals. After 10 min, a solution was made up of 3.60 g AA, a certain amount of MBA and SA, and 10 ml of water. The polymerization process was finalized by keeping the water bath at 80 °C for 3 h. The resulting product was transferred into sodium hydroxide aqueous solution (2 M) to be neutralized to pH 7, and then the samples were spread on a dish to dry to a constant weight at 70 °C in an oven. All the samples used for the test had a particle size of 40–80 mesh after being milled. Table 1 contains the feed compositions of every sample. To examine how introduced SA changes the properties of the superabsorbent, ACN-g-PAA (without SA) was prepared using the same procedure.

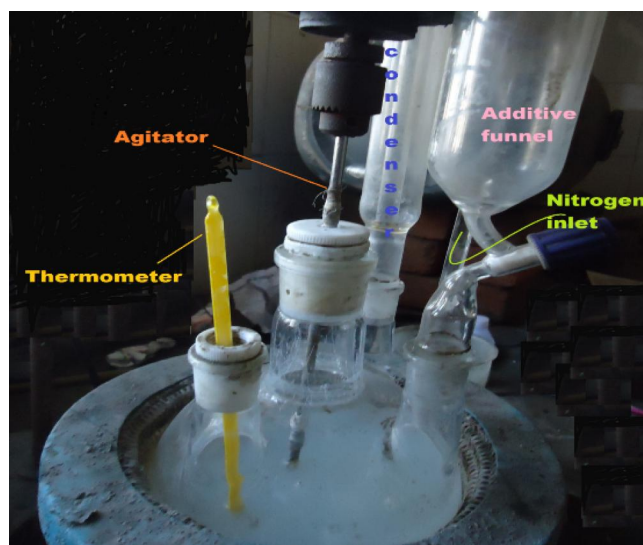


Figure 1. Assembly set for polymerization process.

Table 1. Composition of ACN-g-PAA/SA for preparation of superabsorbent.

Sample notation	AA (g)	ACN (g)	KPS (g)	MBA (g)	SA (g)
Control	3.60	0.50	0.130	0.150	0.00
SAP A	3.60	0.50	0.130	0.150	0.25
SAP B	3.60	0.50	0.130	0.150	0.50
SAP C	3.60	0.50	0.130	0.150	1.00
SAP D	3.60	0.50	0.130	0.150	1.75
SAP E	3.60	0.50	0.130	0.150	2.75

2.3. Measurement of water absorbency

To obtain swelling equilibrium, a sample of 0.05 g was immersed in 50 ml of excess distilled water at room temperature for 4 h. Separation of swollen samples and unabsorbed water was achieved by filtering through a 100-mesh screen under gravity for 10 min without any blotting of samples. The water absorbency in distilled water of the superabsorbent was calculated using the following equation (Equation (1)).

$$Q_{eq} = \frac{m_2 - m_1}{m_1} \quad (1)$$

Where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. Q_{eq} is calculated as grams of water per gram of sample. Water absorbency of the sample in 0.9 wt% NaCl solution, Q'_{eq} , was tested according to the same procedure.

2.4. Application of the sample of non-woven cotton

The core, which absorbs the fluid, was prepared with the cotton fluff-carded web as per the required mass per unit area. The carded web of cotton was coated with all prepared and suitable (in concern with TGA and pH) polymers using a two-bowl padding mangle with a two-dip, two-nip technique (Figure 2).

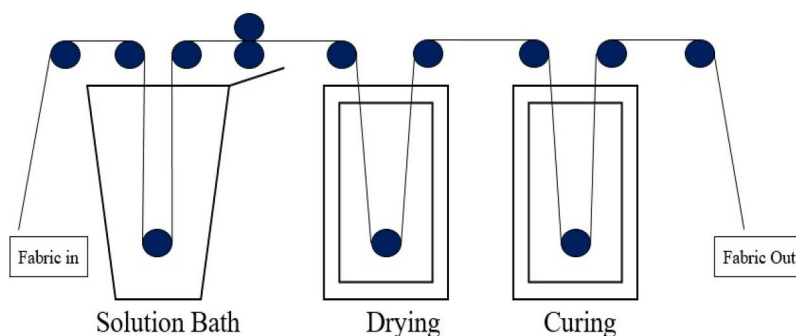


Figure 2. Application of prepared polymers on cotton fluff.

2.5. Free swelling capacity (FSC)

This test measured water absorption in the sample under freely swollen conditions. The tea-bad method is the most convenient and fastest for samples with limited quantities (W_0) (Capezza et al., 2019). A tea bag was used to dip the padded sample in water or a saline solution for an hour. The tea bag was weighed (W_1) again after it had fully swollen, and the swelling capacity was determined using the formula below:

$$FSC = \frac{W_1 - W_0}{W_0} \quad (2)$$

2.6. Absorption under load (AUL)

AUL is used to measure the absorption of the fluid by polymer under a specific pressure. To ensure an even bed, a polymer sample of 0.9 g was distributed evenly on the filter screen. A piston made of aluminum was placed on top of the bed. W_1 is the weight of the entire assembly. A tray was used to hold a porous disk, disk, and tap water and saline solution were added. The whole assembly was placed on the filter paper with a load (0.3 psi) (Bachra et al., 2020). The porous disk was kept in a tray and then filled with tap water and saline solution. Once the given time was up, the assembly was lifted, the load was taken off, and then the cylinder was weighted as W_2 . The AUL was computed using the following equation:

$$AUL \left(\frac{g}{g} \right) = \frac{W_2 - W_1}{W_1} \quad (3)$$

2.7. Test for TGA (thermogravimetric analysis)

Set the nitrogen and oxygen gas flow rates to provide a heating rate of 20 K/min. Place 1.0 g of sample polymer material in the specimen holder and raise the furnace temperature. Set the initial weight (1.0 g) reading to 100%, and then initiate the heating program. TGA measures the mass change in the sample, and it is used to detect evaporation, decomposition, oxidation, and other effects of temperature change that cause mass changes. Data are recorded as a plot of percent weight loss versus temperature (Prime et al., 2009).

TGA investigations of sodium alginate, guar gum, their mixtures, and the polymeric thickeners were carried out with 1.0 g of initial sample material at a heating rate of 20 K/min using the Parkin-Elmer TGA model 4000.

2.8. Moisture content (MC)

An electrically heated oven at 105 °C with normal atmospheric conditions was used for three hours to keep the prepared samples warm and measure the weight loss and dehydration of the samples. Empty dish and covered were followed by the above process, and their weight was noted as M_1 (Bachra et al., 2020; European Disposables and Nonwovens Association [EDANA], 2019). The weight of 4 g of samples was designated as M_2 , and they were spread on the surface of the dish evenly. The arrangement was placed in an oven at 105 degrees Celsius for a duration of 3 h. In the end, the weight was determined to be M_3 . The MC (%) was calculated as follows:

$$MC (\%) = \frac{M_3 - M_2}{M_2 - M_1} \times 100 \quad (4)$$

2.9. Absorbent capacity

The EAS 96:2008-Annex C standard test procedure was used to measure the absorption capacity to evaluate an SAP's absorbency and absorption speed. To achieve saturation, a 0.9% saline solution was added to the dry weight of the SAP-coated pad. Once the pad was saturated, a weight of 3.4 kg was applied to it. The use of filter paper resulted in the soaking of excess fluid, and the pad's weight was measured. Here, saline solution was taken in place of blood (Mukhila & Amrutha, 2023; Yadav et al., 2016). For measuring, the formula shown in Equation (5) was used.

$$Absorption \text{ Capacity } (A) = (W - X)g \quad (5)$$

Where X = dry weight of the pad in grams

W = weight of the pad underweight in grams after saturation

2.10. Rewet back

The test assesses the capability of the SAP-coated sanitary napkin to transport liquid that has flooded the coverstock to

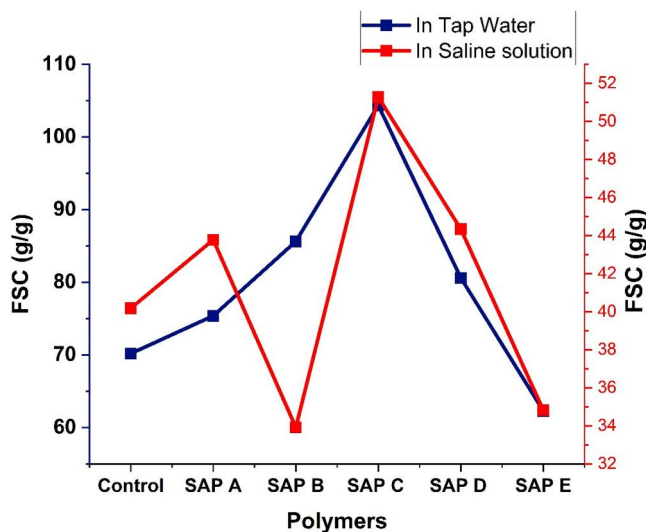


Figure 3. FSC analysis for polymer coated samples.

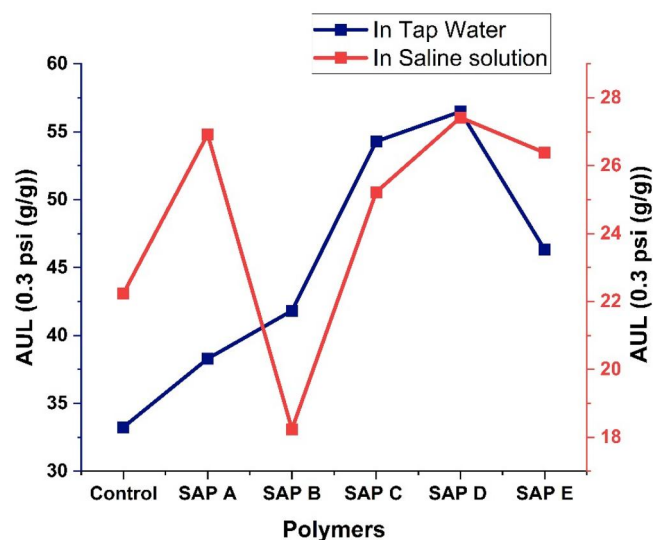


Figure 4. AUL analysis for polymer coated samples.

the skin. The center of an SAP-coated sanitary napkin was soaked in 0.9% saline solution during this test, and it took a minute for the solution to settle. Then, for 15 s, dry filter paper noted as the first, weighing about 3 g, was put at the center. The same process has been repeated for another filter paper noted as the second. The test was carried out on all the samples that were prepared, and the difference between the first and second filter paper was measured (EDANA, 2018).

2.11. Strike through

To conduct the test, a drop of 5 mL of solution (0.9% saline solution) is applied, and the penetration time is measured. A drop of test solution is allowed to free fall on the SAP-coated napkin, and the time was measured for the solution to absorb from the top layer to the inner layer (EDANA, 2018).

3. Result and discussion

Figures 3 and 4 depict the free swell capacity (FSC) and absorption under load (AUL) of SAP in tap water and saline solution. SAP C is credited with the sample having the highest FSC value at 104.35 g/g, while SAP E has the lowest value. The values of SAP A, SAP B, and SAP D are in line with each other. In saline water, the FSC value is a little lower than the value obtained from tap water. Sample SAP C accounts for 51.28 g/g, while the other samples are between 33.92 and 44.34 g/g. The composition of SA with 1.00 g in the SAP matrix suggests the best FSC result compared to the matrixes prepared with other altered concentrations of SA. Which clearly indicates that a higher amount of SA is affecting the FSC, as well as that lower amounts of SA also affect the FSC values. So, the optimum concentration of sodium acrylate (SA) required for preparing SAP for the most suitable FSC result is 1.00 g to 3.60 g of AA and 0.50 g of ACN.

Figures 3 and 4 demonstrate that the AUL values for every sample are lower than the FSC values. Tap water has

values between 33.25 and 56.48, while saline solution has values between 18.24 and 27.42. The market situation shows that thinner hygiene products with less fluff and more SAP are in demand. AUL has a limit on the SAP content of hygienic materials. The accepted value for the hygiene industry is currently 18 to 30 g per gram, but it has the potential to be increased to 50 g per gram. The present study finds that saline solutions have a lower absorption capacity than tap water. The electrolyte in a saline solution can have an impact on the absorption properties of SAP, which are influenced by the presence of ions in water. That is known as the 'charge screening effect', or 'Debye screening', which is due to a greater number of NaCl cations present in saline solution compared to tap water (Fang et al., 2018; Klinpituksa & Kosaiyakanon, 2017; Likhitha et al., 2014), and does the osmotic pressure difference decrease between the SAP network and the solution. In this effect, the sodium ions arrange around the charged particles, with positive ions around positively charged particles and negative ions around negatively charged particles. The net charge of the particle is reduced as a result of this impact. A decrease in the effective charge of the particle is brought about by the charge screening effect. The screening length of a solution with a high concentration of salt is relatively short, but the screening length of a solution with a lower concentration of ions is significantly longer. So, the absorption properties of SAP can be influenced by the electrolytes found in saline solutions, which are influenced by how much water possesses ions.

TGA is a significant measure for the study of the storage capacity of the SAP-coated feminine napkins. After preparation, they may be transported *via* various means, and all the means have a different atmospheric condition. So the stability of the top layer, which is coated with SAP, against temperature should be analyzed, and hence TGA is characterized for the prepared SAPs. Figure 5 validates that the polymer SAP C has excellent thermal stability until 340 °C, but the sample lost 14% of its weight at this temperature. Due to moisture traces in the polymer, an initial weight loss was observed.

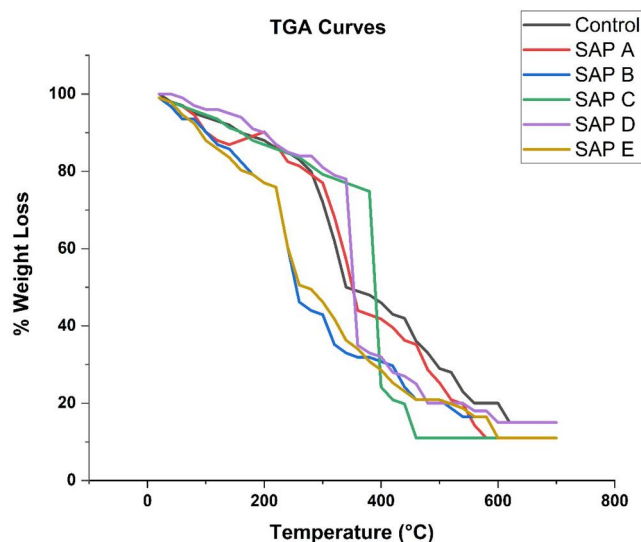


Figure 5. TGA curves of all formulated SAPs.

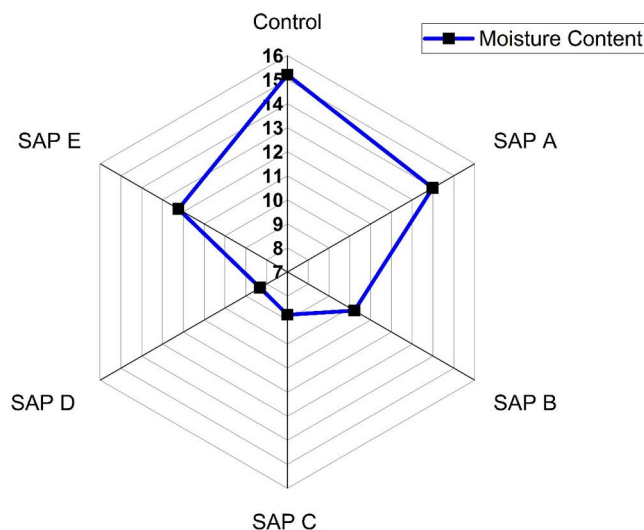


Figure 6. Moisture content of all SAPs.

Polymer SAP C's weight loss was slower, with almost 72% of it observed at 380 to 420 °C. Despite being a synthetic polymer, the product slowly breaks down its polymer backbones at higher temperatures. All other polymers and the control one have a higher weight loss compared to SAP C in the range of 200–380 °C, while SAP D indicates a range of 360–380 °C for effective weight loss. In the study, high-molecular-weighted SAPs show initially higher stability in the series, but at the end they show lower stability. As the molar ratio of SA increases, the thermal stability decreases, and at a lower concentration of SA, the stability is higher. For the optimum concentration of SA (1.0 g), the most suitable stability has been achieved for storing, transporting, and logistically stable SAP-coated napkins.

The samples were treated in an oven at 105 °C for 3 h, and the results of the calculation are displayed in Figure 6. The controlled sample achieves the greatest MC value of 15.2 weight%, whereas SAP D displays the lowest value. According to studies reviewed, the absorption capacity decreases when SAP is manufactured due to disruptions related to MC. It has been suggested by some studies that

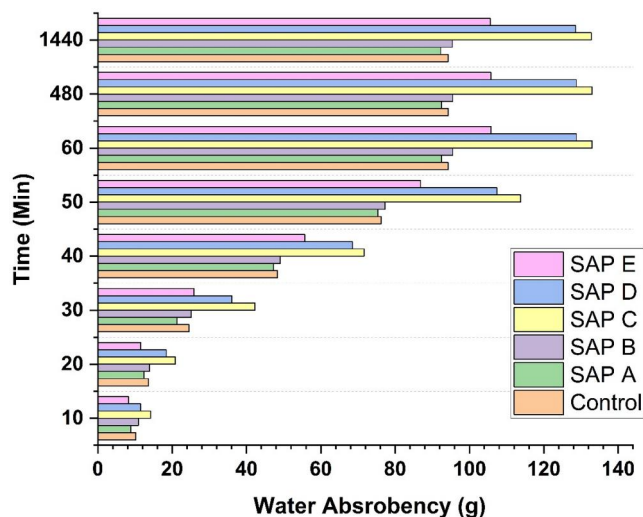


Figure 7. Water absorbency of SAPs at different time interval.

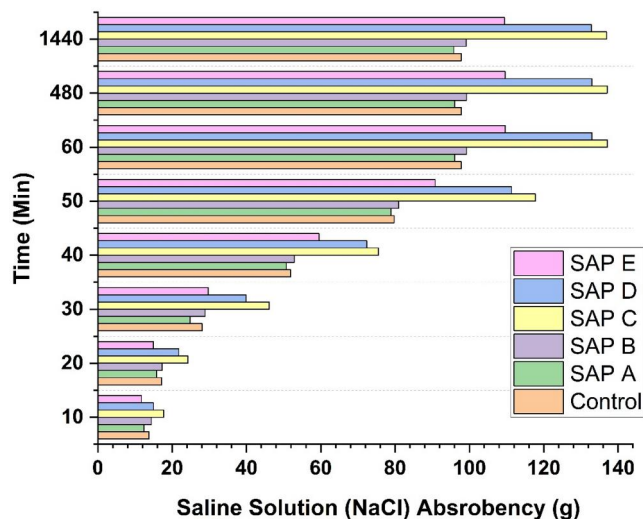


Figure 8. Saline solution absorbency of SAPs at different time interval.

MC between 5 and 15% is the most ideal. All the prepared polymers received identical results in this work.

Figures 7 and 8 reveal the water absorption capacity of individual hygiene products for tap water and saline solutions. It's clear from Figure 7 that SAP C has the highest absorption capacity after 10 min. The weight can range from 14.24 g to 132.97 g in a range of 60 min to 8 h. The SAP C-coated feminine napkin suggests that the maximum amount of water absorbed is 132.78 g for 24 h. While for other products, it is 8.23, 8.9, 10.24, 10.89, and 11.48 g of water absorption for SAP E, SAP A, SAP B, and SAP D, respectively, at the interval of 10 min. Figure 8 suggests that a polymer-coated feminine napkin can absorb the saline solution. Additionally, it aids in the results of tap water absorption. The SAP C-coated feminine diaper has the most efficient absorption of saline solution, 134.09 g, over the course of 60 min to 8 h. Control, SAP A, SAP B, SAP D, and SAP E samples indicate that 94.84, 93.01, 96.24, 129.97, and 106.64 g of saline solution were absorbed while under control. Both figures support the SAP C for tap water and saline solution absorbency, which increases continuously for 8 h before remaining nearly constant for 24 h. It

clearly suggests that the napkins coated with SAPs are significantly absorbing the fluid with each increment in time; at the specific interval of time, it became constant. So, after 8 h, the napkin must be changed as it will not absorb more fluid after the said time.

The test is executed to evaluate the wetness level of the sanitary napkin, which can hinder the transfer of fluid to the skin from the napkin when it absorbs onto the coverstock. The performance analysis of samples coated with control and SAPs can be easily seen in Figure 9. In terms of wet-back properties, the control sample is superior to the SAP-A and B-coated sanitary napkins. While SAP-C suggests 0.2 g at first wet and 0.1 g at second wet, which are the most promising values comparable to

commercially available sanitary napkins taken as control samples, SAP-D and SAP E's wet back properties differ slightly, and they are displaying higher values at a lower level than SAP-C and control. Excellent wet-back properties in SAP-C can be attributed to the ratios of AA, ACN, and SA, respectively. Variation in the wet back result is happening to other shops because of the change in the ratio of their composition used for preparing polymers.

A strike-through test is used to measure the speed of a fluid's transport from the surface it absorbs to the inner zone of the pad. The increase in strike-through indicates that the pad's top layer is quickly absorbing the fluid, which results in dry skin. Figure 10 suggests that the control sample has a higher speed of transportation, and so the time required for passing the fluid from the surface to the inner part is less than 2.58 s. The napkin with the top layer coated with SAP-C required fluid transportation within 2.32 s. Poor strike-through properties were a result of the SAP-B-coated layer taking the longest. The time for striking in SAP A, SAP D, and SAP E is approaching. SAP-prepared pads lead to an increase in strike-through. Because of the hydrophilicity of cotton and the absorbency capacity of SAPs, the presence of cotton and needle-punched cotton at the top layer in prepared samples suggests a comparable strike-through property.

The absorption capacity of a napkin that had SAP-coated cotton on the top layer was compared to the control napkin on the market. The control sample shows that 63.4 g of saline solution were ingested. In Figure 11, it can be seen that the SAP-C layer on top of the napkin absorbs exactly 63.72 g, which is similar to the outcome of sanitary pads sold on the market. SAP E, SAP B, and SAP D sanitary napkins are less expensive than SAP-C-coated ones, with values of 60.89, 62.28, and 62.32, respectively, in incremental order.

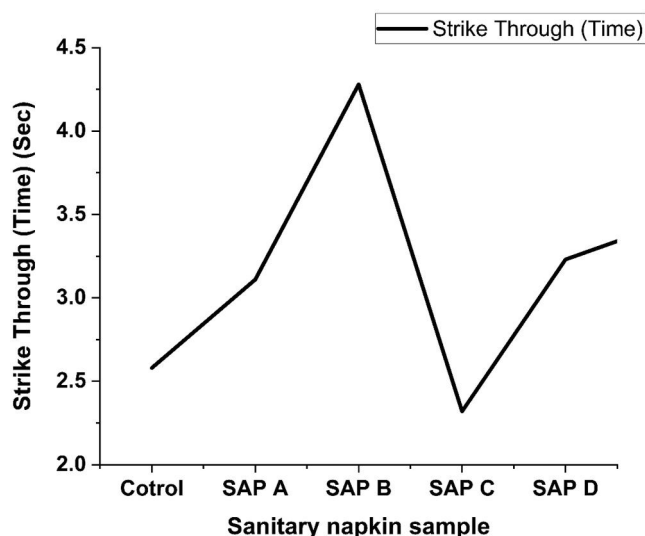


Figure 9. Strike through (time) from samples.

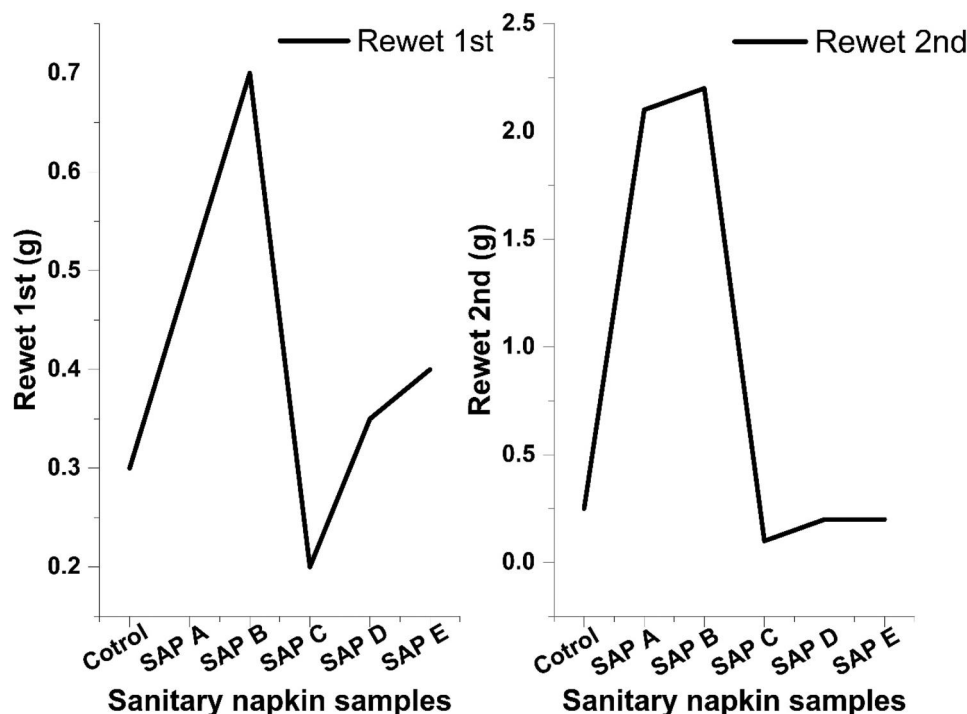


Figure 10. Rewetting of samples.

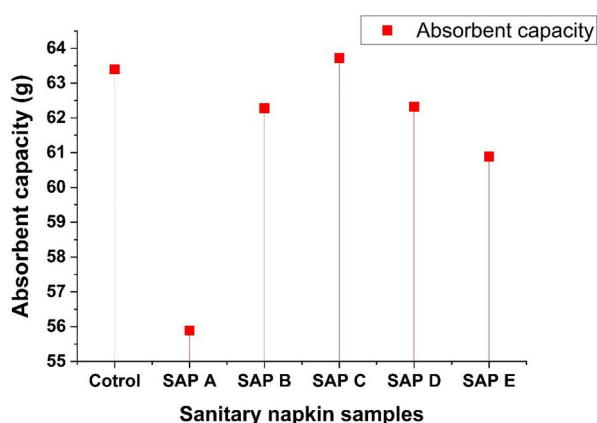


Figure 11. Absorbent capacity for the samples.

SAP-A is less effective at absorbing saline solutions than other shapes and control samples. The control sample's higher absorption values are a result of the presence of super-absorbent polymers and cotton pulp. The acrylate-based polymer prepared for research was coated with needle-punched cotton that was adjusted to the top layer and experienced the same phenomenon. The SAP-coated napkins can replace the control ones due to their higher absorption.

4. Conclusion

To make a cheaper feminine napkin compared to available market products and also to improve the performance of the same product, which is in huge demand, the addition or coating of SAP is the best suitable for achieving all the above-mentioned purposes.

Preparation of poly (acrylic acid)/sodium acrylate (ACN-g-PAA/SA) and then application on the top layer of a feminine napkin was practically performed, and the analysis of the same coated product with a commercially available napkin was also done. The cotton carded web coated with SAP A to E was tested in terms of various performance analyses, and from all the results, it has been concluded that cotton carded when coated with SAP C is most suitable for feminine hygiene, with the highest FSC values in both tap water and the saline solution. When it comes to AUL, SAP D is the top choice for tap water, while SAP B is not recommended for saline solutions, as it suggests lower absorption. SAP C was also suggested by the moisture content analysis. The TGA curve supports polymer SAP C as well. Also, absorbance capacity, reset, and strike through support the SAP C-coated top layer of feminine hygiene. And so, SAP C is the most suitable polymer product for coating the top layer of sanitary napkins, in comparison to commercially available products.

The problem with the prepared SAP is its biodegradability. So, the same polymer can be synthesized by grafting natural polymers to improve biodegradability and reduce toxicity. Also, other monomers can also be utilized for preparing SAP for application in feminine hygiene by coating, laminating, or surface modifying.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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