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Sardorbek KARIMOV,
PhD, professor, Toshkent to‘qimachilik va yengil sanoat instituti, Toshkent, O‘zbekiston
E-mail:sssskarim81@gmail.com. ORCID 0000-0001-9201-5653
Adham RAFIKOV,
Kimyo fanlari doktori, professor, Toshkent to‘qimachilik va yengil sanoat instituti, Toshkent, O‘zbekiston
Sunnatullo MURADOV,
Mustaqil izlanuvchi, Toshkent to‘qimachilik va yengil sanoat instituti, Toshkent, O‘zbekiston
Azimbay REYIMOV,
PhD, dotsent, Toshkent to‘qimachilik va yengil sanoat instituti, Toshkent, O‘zbekiston

PhD., dotsent A.Iskandarov taqrizi asosida

SERITSINNI AKRIL MONOMERI BILAN PAYVAND SOPOLIMERLANISHI VA FIZIK-KIMYOVIY TAHLILI

Annotatsiya

Tabiiy ipak chiqindilaridan ajratib olingan seritsin oqsilining akril kislorasi bilan kaliy persulfat inisiatori ishtirokida payvant sopolimerlanish jarayoni o‘rganildi. Reaksiya davomida seritsin makrozanjiriga poliakrilat segmentlari kovalent bog‘lanishi natijasida yangi sopolimer hosil bo‘ladi. Olingan mahsulotning kimyoviy tuzilishi IQ-, ^{1}H PMR va ^{13}C PMR spektroskopik usullar yordamida tahlil qilindi. Tahlillar shuni ko‘rsatadi, spektrlarda dastlabgi namuna va hosil bo‘lgan sopolimerlarida funksional guruhlariga xos signal va yutilish chiziqlarining o‘zgarishi sopolimerlar hosil bo‘lganligini ko‘rsatadi. Xususan, karboksil guruhlari signallarining ortishi va yangi bog‘lanishishlarning paydo bo‘lishi poliakrilat monomerlari seritsin tarkibiga birikkanligini hamda yangi funksional guruhlariga ega ekanligini ko‘rsatadi.

Kalit so‘zlar: seritsin, akril monomerlari, payvand sopolimerlanish, IQ- spektr, PMR- spektr.

ПРИВИВОЧНАЯ СОПОЛИМЕРИЗАЦИЯ СЕРИЦИНА С АКРИЛОВЫМ МОНОМЕРОМ И ФИЗИКО-ХИМИЧЕСКИЙ АНАЛИЗ

Аннотация

Изучен процесс привитой сополимеризации белка серицина, выделенного из отходов натурального шелка, с акриловой кислотой в присутствии инициатора персульфата калия. В ходе реакции образуется новый сополимер в результате ковалентного связывания полиакрилатных сегментов с макроцепью серицина. Химическую структуру полученного продукта анализировали методами ИК-, ПМР ^{1}Н и ПМР ^{13}С. Анализ показывает, что изменения в спектрах сигналов и линий поглощения, характерных для функциональных групп исходного образца и полученных сополимеров, свидетельствуют об образовании сополимеров. В частности, увеличение сигналов карбоксильных групп и появление новых связей свидетельствуют о том, что мономеры полиакрилата присоединяются к серицину и имеют новые функциональные группы.

Ключевые слова: серицин, акриловые мономеры, прививочная сополимеризация, ИК-спектр, ПМР-спектр.

GRAFTING COPOLYMERIZATION OF SERICINE WITH ACRYLIC MONOMER AND PHYSICOCHEMICAL ANALYSIS

Annotation

The process of graft copolymerization of sericin protein isolated from natural silk waste with acrylic acid in the presence of potassium persulfate initiator has been studied. During the reaction, a new copolymer is formed as a result of covalent binding of polyacrylate segments to the sericin macrochain. The chemical structure of the resulting product was analyzed by IR, 1H PMR and 13C PMR methods. The analysis shows that changes in the spectra of signals and absorption lines characteristic of the functional groups of the initial sample and the resulting copolymers indicate the formation of copolymers. In particular, the increase in carboxyl group signals and the appearance of new bonds indicate that polyacrylate monomers are attached to sericin and have new functional groups

Keywords: sericin, acrylic monomers, graft copolymerization, IR spectrum, PMR spectrum.

Kirish. Xozirgi kunda sanoat, ishlab chiqarish mahsulotalari chiqindilaridan rasional foydalanish, ular asosida turli sohalar uchun muxim bo‘lgan kimyoviy birikmalar ishlab chiqarish ham ekologik nuqtai nazardan, ham iqtisodiy jihatdan yuqori samara beradi. O‘zbekiston Respublikasi Prezidentining “Chiqindilarni qayta ishlashni yanada takomillashtrish” to‘g‘risidagi PF-56 sonli farmoniga muofiq, tabiiy polimer moterial Ipak ishlab chiqarish sanoatida ko‘plab serisin chiqindilari tashlab yuboriladi. Tabiiy ipakning muhim tarkibiy qismida serisin bo‘lib, uni ajratib olgan holda maqsadli foydalanish mumkin.

Seritsin oqsili ipak pillasidan olingan oqsil turidir. Seritsinning vodorod bog‘lari ipak pillasiga bog‘lanadi . Ushbu modda o‘z tarkibida ko‘p miqdordagi serin aminokislotalarni o‘z ichiga oladi. Dastlab, bu moddaning dorivor xususiyatlari kashf etilgan. Serisinning noyob xossalari uni to‘qimachilik, farmasevtika va kosmetika sanoatida keng qo‘llash imkonini beradi [1-4].

Tabiiy ipak chiqindilaridan ajratib olingan serisinni kimyoviy yo‘l bilan modifikasiya qilinayotgan materialning tolalariga bog‘lanishini ta’minlash kerak. Turli monomerlarni serisinga, serisinni monomerlar orqali material tolalariga payvand sopolimerlash maqsadga erishishning samarali usullaridan biridir.

Tadqiqotlarning dastlabki bosqichida tabiiy ipak tarkibidan serisinni imkoni boricha toza birikma holida ajratib olishga erishildi.

Materiallar va metodlar

IQ spektrining skanerlovchi sohasi qattiq, suyuq, gelsimon va qayta ishlash qiyin bo‘lgan moddalarni tahlil qilishga mo‘ljallangan 4000-400 sm^{-1} oralig‘ida o‘rganildi. Polimerlarning eruvchanligiga qarab erituvchi tanlanadi. Oqsillar va gidrogellar uchun odatda og‘ir suv (D_2O) yoki "dimetilsulfoksid" (DMSO-d_6) ishlariladi. Uskuna: ^1H NMR spektrlari Bruker Avance (odatda 400 yoki 500 MHz) spektrometrida yozib olindi.

Namunani tayyorlash: Taxminan 10-15 mg polimer namunasi 0.6 ml erituvchida (D_2O yoki DMSO-d_6) to‘liq eritildi va 5 mm li NMR ampulasiga o‘tkazildi.

O‘lchash parametrlari: Spektrlar 298 K (25°C) haroratda olindi. Kimyoviy siljishlar (δ, ppm) ichki standart – tetrametilsilan (TMS) yoki erituvchining qoldiq proton signaliga nisbatan hisoblandi.

^{13}C NMR spektrlari xuddi shu Bruker Avance uskunasida (100 yoki 125 MHz chastotada) yozildi.

Natijalar va ulrning tahlili

Tabiiy ipakni qayta ishlash korxonalaridagi ishlab chiqarishda mahsulotlari tarkibini fibroin, serisin va shunga o‘xshash oqsillar tashkil etadi. Ajratib olingan serisin tarkibida 15 dan ortiq aminokislotalar uchraydi. Bu aminokislotalardan tashkil topgan oqsillar kuchsiz ishqoriy muhitda gidrolizga uchrashidan foydalanib, serisin oqsillarini natriy gidrokarbonat, ho‘jalik sovuni vannasini tashkil etib, tabiiy ipak eritildi.

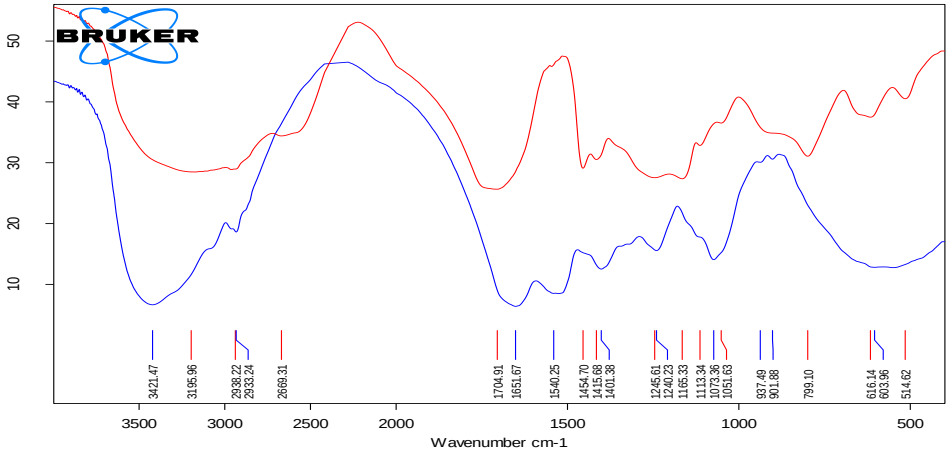
Tajribalardan ma’lum bo‘ldiki natriy gidrokarbonat, ho‘jalik sovuni vannasini konsentrasiyasining ortishi bilan serisinning erishi kuzatildi. Kuchsiz ishqoriy muhitda molekulalararo bog‘larning uzilishi va oqsilning qisman gidrolizlanishi sodir bo‘ladi.

Olingan serisinni akril monomeri bilan payvand sopolimerlanishi jarayoni suvda inisiatorlar ishtirokida o‘rganildi.

Akril kislotasini suvli eritmada kaliy persulfat ishtirokida ishtirokida payvand sopolimerlanish jarayonining sodir bo‘lishi aniqlandi.

Kaliy yoki ammoniy persulfatlar [4-10], vodorod peroksid [11], tetra valent seriy ionlari [12-14], tsellyuloza atsetilxlorid [15, 16], benzoil peroksid [17] va boshqalar ishtirokida payvand sopolimerizatsiyasining boshlang‘ich markazlari hosil bo‘ladi. Seritsinning PAK kislotasi bilan payvand sopolimerlanish jarayonida kaliy persulfat ishtirokida amalga oshirildi. Shuni xisibga olgan xolda seritsinning IQ- spektrini o‘rganimizda funksional guruhlarining xarakteristik tebranish chastotalari 3421,47 sm^{-1} NH valent bog‘lari, 2933,24 sm^{-1} assimmetrik valent, 1651,67 sm^{-1} –N=O valent, 1540,25 sm^{-1} NH^{3+} assimetrik deformatsion bog‘larning tebranishlarini ko‘rishimiz mumkin. Ushbu holatda sopolimerlanish jarayonida sohalarning qo‘zg‘aluvchan holatlarini hamda sintezda ishtirok etish uchun amalga oshirildi. Payvand sopolimerlanish reaksiyasidan keyin quyidagi sintez tahlil qilindi[18, 19].

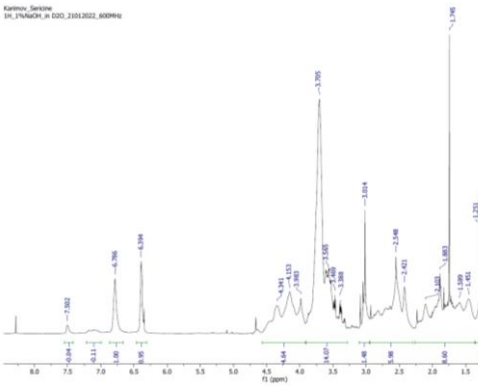
Seritsinni akril kislotasi bilan payvand sopolimerlanish IQ- spektrini ko‘radigan bo‘lsak, Seritsinning IQ- spektrida 2500-3000 sm^{-1} yutilish sohasida o‘zgarish kuzatilganini ya’ni seritsinning akril monomeri bilan payvand sopolimerlanish IQ- spektrida 2669,31 sm^{-1} yutilish sohasida yangi NH^+, NH^{2+} va NH^{3+} ionlarining valent bog‘lari paydo bo‘lganligini, jumladan akril kislotasining IQ- spektridagi 1600 sm^{-1}-1640 sm^{-1} $=CH_2$ qo‘sh bog‘larini yutilish sohalari ko‘rinmay, polimerlanib poliakrilatlarga aylanganligi (rasm-1) bildiradi.



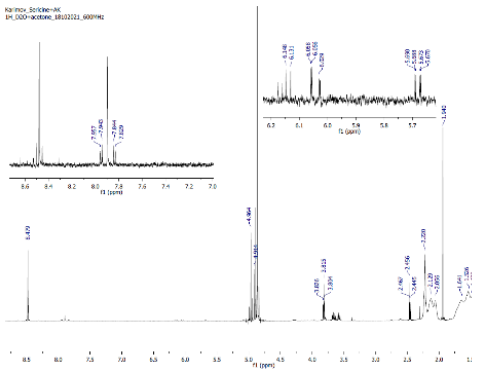
rasm-1 Seritsin va seritsinning poliakril kislotasi bilan payvand sopolimerining IQ- spektri

Shu jumladan (rasm-2) serisinning ^1H PMR- spektrini ko‘rib chiqadigan bo‘lsak, Spektrdagi sohalar seritsin tarkibidagi aminokislotalarning qoldiqlariga xosdir: 0.8 – 1.5 ppm oralig‘i, bu sohada metil (-CH_3) va metilen (-CH_2-) guruhlarining protonlari namoyon bo‘ladi. Alanin (CH_3) va valin kabi aminokislotalarning signallari shu yerda joylashgan. 3.5 – 5.0 ppm oralig‘ida esa polipeptid zanjiridagi -protonlar (H-α) va serin aminokislotasining yon zanjiridagi (CH_2-OH) protonlar sohasidir. Seritsin seringa juda boy bo‘lgani uchun bu sohadagi yutilish chiziqlari juda intensiv bo‘ladi. 6.5–8.5 ppm oralig‘ida aromatik halqali aminokislotalar tirozin va peptid bog‘idagi amid (NH) protonlari sohalari ko‘rishimiz mumkin.

Seritsinni PAK bilan payvand sopolimerlanish ^1H PMR- spektrini ko‘radigan bo‘lsak (rasm-3), poliakril kislota (PAK) zanjirining namoyon bo‘lishi, spektrning 2.0–2.5 ppm va 1.3–1.8 ppm sohalaridagi yangi va intensiv sohalar paydo bo‘lganligini, 2.220 ppm atrofidagi cho‘qqilar PAK asosiy zanjiridagi –CH– guruhiga tegishli, 1.4–1.6 ppm sohasidagi keng signallar esa PAK zanjiridagi –CH_2– guruhlari vodorodlariga xosdir.



rasm-2 Seritsinning ^{1}H PMR- spektri

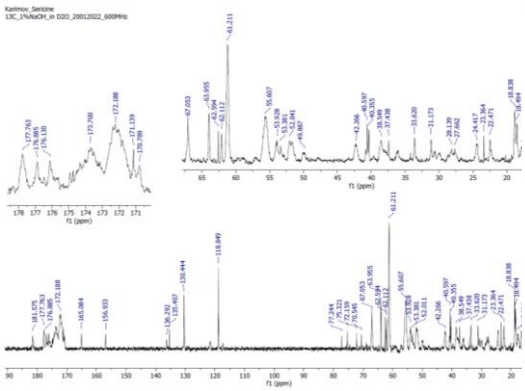


rasm-3 Seritsinning poliakril kislotasi bilan payvand sopolimerining ^{1}H PMR- spektri

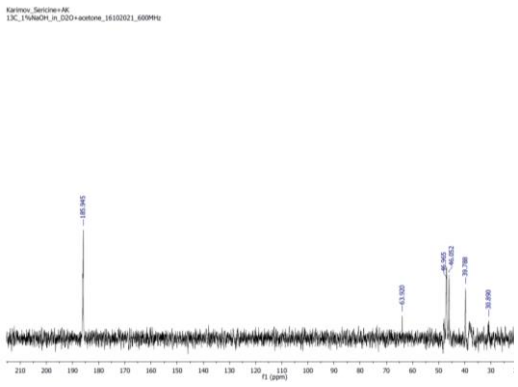
Seritsinning o‘zida bu sohalar bunday intensivlikda bo‘lmaydi, bu esa tizimga polimer zanjiri kirganini ko‘rsatadi. Payvandlanish bog‘larining dalili sopolimer hosil bo‘lishi ko‘pincha seritsinning aminokislota qoldiqlaridagi aktiv markazlar lizin/amid guruhlari orqali amalga oshadi. 4.9-5.0 ppm va 3.8-4.0 ppm sohalaridagi o‘zgarishlar serin qoldig‘idagi –CH_2–OH guruhining modifikatsiyalanganini ya’ni eterifikatsiya yoki efir bog‘i hosil bo‘lganligini bildiradi. 4.479 ppm sohasidagi kuchli signal amid –NH– protonlariga tegishli bo‘lib, payvandlanish jarayonida peptid zanjiri saqlanib qolganini va ehtimol yangi amid bog‘lari hosil bo‘lganini anglatadi.

Toza komponentlardan farqi, agar bu shunchaki mexanik aralashma bo‘lganida, har bir komponentning signallari alohida-alohida o‘zgarmasdan ko‘ringan bo‘lardi. Spektrdagi yutilish chiziqqlarning bir-biriga multipletlikning murakkablashishi va kimyoviy siljishlarning biroz o‘zgarishi kimyoviy kovalent bog‘ hosil bo‘lganidan dalolat beradi. 5.6-6.2 ppm sohalar tasvirning tepa qismidagi kattalashtirilgan sohada ko‘rinayotgan yutilish chiziqlari 5.688, 6.058, 6.131 ppm reaksiyaga kirishmagan akril kislota qoldiqlari yoki zanjir oxiridagi qo‘shbog‘li (C=C) protonlar bo‘lishi mumkin. Ularning intensivligi pastligi reaksiyaning yuqori darajada amalga oshganini ko‘rsatadi.

Keyingi jarayonda ya’ni sopolimer xosil bo‘lganini isbotlash uchun seritsinning ^{13}C PMR- spektrini o‘rganganimizda (rasm-4) seritsin asosan serin, glitsin va asparagin kislotadan iborat. Spektrdagi asosiy yutilish chiziqlari (signallar) quyidagicha guruhlangan karbonil guruhlari (C=O) 170–182 ppm sohasida, peptid bog‘laridagi (CONH) karbonil uglerodlari 172-174 ppm sohalarida, asparagin va glutamin kislotalarining yon zanjiridagi karboksilat (-COO^-) guruhlari, tirozin aminokislotasining aromatik halqasidagi uglerodlar 118.8, 130.4 ppmda, serin uchun eng xarakterli cho‘qqi 61-63 ppmda, aminokislotalarning C_α uglerodlari 50-57 ppm sohasida, glitsinning C_α uglerodi 42-43 ppm yutilish chizig‘ini, alaninning metil guruhi (-CH_3) sohalrini ko‘rishimiz mumkin.



rasm-4 Seritsinning ^{13C} PMR- spektri



rasm-5 Seritsinning poliakril kislotasi bilan payvand sopolimerining ^{13}C PMR- spektri

Jumladan (rasm-5) Seritsinning poliakril kislotasi bilan payvand sopolimerining ^{13}C PMR- spektri ko‘radigan bo‘lsak yangi kimyoviy bog‘ 185.9 ppm akril kislotasining (C=O) karbonil guruhining seritsin zanjiriga birikkandan keyingi holat, 63.9 ppm yutilish chizig‘i seritsindagi serin qoldig‘ining (–CH_2-OH) guruhi inisiator ta‘sirida ehtimol AK bilan efir hosil bo‘lgan bo‘lishi mumkin. 20-50 ppm sohalarida alifatik soha (–CH_2–) va (–CH–) guruhlari signallariga to‘g‘ri keladi.

Olingan natijalar shuni ko‘rsatadiki, poliakril kislota zanjiriga xos alifatik protonlar va seritsin oqsiliga xos signallarning bir vaqtda mavjudligi hamda ularning o‘zaro ta’siri seritsin-g-PAK payvand sopolimeri muvaffaqiyatli sintez qilinganini isbotlaydi. Bu esa ipak sanoati chiqindilaridan yuqori samarali polimer materiallar olish imkonini beradi.

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