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Electrospinning of Fatty Acid-Based and Metal Incorporated Polymers for the Fabrication of Eco-Friendly Fibers



Ecologically benign macroperoxide nanocomposite inititator was used in free radical polymerization of metal loaded and fatty acid-based vinyl monomer via autoxidation. The obtained graft copolymers were successfully processed by electrospinning for the fabrication of continuous fibers. PMMA and PS fibers with ricinoleic acid and Ag nanoparticles show notable antibacterial activity against Gram negative bacteria (*E. coli*).



Electrospinning of Fatty Acid-Based and Metal Incorporated Polymers for the Fabrication of Eco-Friendly Fibers

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Accumulation of plastic wastes occupies large space in gyres of the oceans called the 7th continent. This high-level concentration of toxic plastic wastes causes harmful consequences for marine life, therefore petroleum-originated plastics must be replaced (or at least partially) with natural resources. The environmental trends in material preparation promote the utilization of greener methods and materials when the limited primary sources are considered. Starting from the fatty acid macroperoxide initiators, synthesis of bio-based polymers using less commercial chemicals and stepwise green synthesis schemes could be possible in the near future. In this research, autoxidized vegetable oil initiators (castor, limonene, and soybean oil) containing metal nanoparticles (silver, platinum, and gold) are employed for free radical polymerization of vinyl monomers. The metal loaded and vegetable oil-based polymers are processed by electrospinning and end up with the successful fabrication of continuous fibers. Ag-loaded ricinoleic acid based polymers show notable antibacterial activity against Escherichia coli. This approach offers a remarkable minimization of the initiator consumption in the synthesis of such synthetic macromolecules as well as nanoparticle containing polymer composites while still maintaining the ease of processing. Transforming the obtained graft copolymers to electrospun nanofibers facilitates the use as support materials for antibacterial surfaces.

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1. Introduction

In the last three decades, polymers have been gaining great attention in a wide range of industrial applications such as aerospace, automotive, marine, medical devices, and even in daily consumer products such as sports and kitchen equipment. Resistance to degradation, low cost, and ease of processing make them privileged among the other materials.^[1] The raw materials for polymer production are supplied by the petrochemical resources and the polymers account for nearly 7% of total petrochemical resource consumption.^[2] However, petrochemical resources are not feasible over the long run because they are sensitive to price fluctuations in the market and are nonrenewable. Moreover, from the sustainability point of view, synthetic polymers are not environmentally friendly because their nondegradable nature poses significant concerns such as air, water, and soil pollution. Although there are environmentally friendly ways to recycle and reuse them,^[3,4] still there is a need for novel polymeric

materials from renewable and sustainable raw materials, which are one of the principles of the green chemistry approach.^[1,5] Oils, polysaccharides, and proteins have been broadly used as renewable resources and oils are one of the most extensively used feedstock because of their abundance in nature as well as their functional properties and low cost.^[6,7] Vegetable oils are found in plant seeds and they are available all around the world. Glycerin and fatty acids with different numbers of carbon atoms and carbon-carbon double bonds constitute the vegetable oils, which are distinguished by the composition of fatty acids. Palmitic, stearic, oleic, linoleic, and ricinoleic are the common fatty acid compositions found in vegetable oils.^[8] Researchers take a close interest in vegetable oils that the possibility of crosslinking the carbon-carbon double bonds in oils through polymerization permits the design of bio-based polymers as an alternative to petroleum-derived products.^[9] The novel and tailor-made compounds have been synthesized in an ecofriendly way by modifying vegetable oils through epoxidation, esterification, and acetylation reactions.^[10] Fatty acids are the main constituents of oils and they are susceptible to autoxidation, which leads to the polymerization of unsaturated moieties through epoxidation, peroxidation, and cyclization.^[11] Free radical polymerization of vinyl monomers is carried out by the formation of macro peroxide initiators, which were synthesized by the autoxidation of dou-

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ble bonds through peroxidation and polymerization.^[12,13] Thus, macro peroxide initiators lead to the formation of fatty acid-poly olefin conjugate biopolymers, and the carboxyl functional group in the fatty acid macro peroxide initiators facilitates the one-pot polymerization.^[14,15] Due to its low cost and abundance, soybean oil is one of the most frequently used renewable resources that autoxidation leads to the formation of peroxide radicals and oxidized fatty acids take place in the free radical polymerization of vinyl monomers through an eco-friendly route, such as styrene and methyl methacrylate.^[16] Castor oil is another commercially available renewable resource and ricinoleic acid (RA) is derived from castor oil used to synthesize biodegradable polymers.^[17]

Biodegradable polymers have made use of especially from medical applications because their nontoxic features and drug delivery systems get the edge on these biodegradable polymers in various pathological cases.^[9] Using fatty acid-based carrier systems can treat intracellular infections and the synthesized biodegradable polymers are highly promising due to their nontoxic and biocompatible nature considering the adverse effects of petroleum-based polymers.^[18] Ghitman et al. synthesized hybrid polymer-vegetable oil nanoparticles by using poly (lactic-coglycolic) acid and Nigella sativa vegetable oil for lipophilic drug delivery and controlled release. The vegetable oil was explored as a carrier matrix through the process.^[19] Castor oil-based microparticles were synthesized by Gallon et al. via sol-gel chemistry and the synthesized particles were tested for potential drug delivery systems using ibuprofen that shows nearly 95% loading efficiency.^[20] The main disadvantage of vegetable oil-based polymers is their lack of mechanical properties due to the long fatty acid chains. The drawback of these bio-based polymers can be overcome by the incorporation of inorganic additives such as metal nanoparticles, metal oxides, and clays.^[18,21-23] Silver nanoparticles (Ag NPs) have a broad spectrum of antibacterial activity due to their disinfectant feature against various microorganisms. The positively charged Ag ions and negatively charged cell membrane of microorganisms interact electrostatically and positively charged Ag ions break the DNA replication by damaging the membrane that results in the death of the cell.^[24,25] Kumar et al. synthesized Ag NPs incorporated paints by using Cardanol oil and a polymer with acrylic backbone, and the resulting resins showed antibacterial properties.^[26] Hazer et al. demonstrated the antibacterial behavior of Ag NPs coated biopolymers, which were synthesized by autoxidation of soybean oil and silver nitrate followed by the polymerization of vinyl monomers. The resulting nanocomposites showed both antibacterial efficiency and high fluorescence emission, promising for imaging specific targets in medical applications.^[27] The vegetable oil-based graft copolymers have been successfully reported in various biomedical applications such as osteogenic differentiation and mineralization, cell proliferation, and cell growth due to their blood protein adsorption and bacterial adhesion features.[28]

Electrospinning offers a great possibility to fabricate continuous nanofibers with extremely long lengths and uniform diameter.^[29–31] The enhanced surface area and controllable porosity enhance the active sites on the fibers and this improved structure enables the utilization of electrospun fibers in various fields such as tissue engineering, drug delivery, and antibacterial surface applications.^[32–37] It gives the impression of being easyto-use and straightforward but it is a rather complicated process that has several processing parameters and configurations, which affect the final structure of fibers. Not only the molecular weight of the polymer, solution concentration, solvent conductivity, solution viscosity, applied voltage, the flow rate of the syringe pump, the shape of the collector, and tip-to-collector distance but also the modification of these parameters are considerably effective on the resulting fiber morphology. The main components of electrospinning are a high voltage supply, a spinneret or conductive needle, a syringe pump, and a grounded collector. The spinneret is fed with the polymer solution, which the syringe pump supplies, and the conductive needle is exposed to a high voltage that results in electrostatic repulsion between charges on the polymer solution. When the electrical field overcomes the surface tension of the polymer solution, the polymer jet is transported through the electrical field and the electrospun fibers are collected on the grounded collector.[38]

The recent interest in organic-inorganic composite fibers has been growing due to the developments in the fabrication of hybrid functional materials. The resulting composite fibrous structures not only show the sum of the individual contributions of components but also improved the advantageous features of material such as their mechanical integrity that the interface between two components takes a significant part in the determination of fiber performance.^[39] Incorporation of the nanoparticles, which might be called nanofillers or nano-inclusions, have been recognized with perfectly active surfaces for various applications such as anticancer treatment,^[40] antimicrobial activity,^[23] catalysis,^[41] drug delivery,^[42] filtration,^[21,22,43] and volatile organic compound sensing.^[44] AgNPs have been frequently used in composite nanofibers due to their optical, catalytic, and biomedical features. Zhang et al. reported the antimicrobial property of Ag incorporated polyvinyl alcohol fibers,[45] whilst Poyraz et al. fabricated Ag incorporated polyaniline nanofibers, which shows antibacterial behavior against Staphylococcus aureus and Escherichia coli.[46] Moreover, many of the fatty acids extracted from plants have known their drug effects and have been used in medicinal applications. Horzum et al. demonstrated the curcumin-loaded bio-based polyurethane electrospun fibers for wound healing applications. Soybean oil derivative is polymerized with acrylate counterparts and thermoset films and fibers were fabricated via photopolymerization. The high carbon content of resulting materials brings to the front biodegradable fibrous materials for further green material applications.^[47]

In this study, the graft copolymers based on polymeric triglyceride/fatty acids containing metal nanoparticles were synthesized. The as-synthesized copolymers were characterized by scanning electron microscope (SEM), Fourier transform infrared (FTIR), ultraviolet-visible (UV-vis), and thermogravimetric (TGA) analyses. Then, they were processed by electrospinning for the fabrication of continuous nanocomposite fibers. Different physical characteristics of polymers end up with various thermal and morphological features. Ag-loaded polymers were electrospun successfully, whilst Pt-loaded polymers cannot be processed with this technique due to their low solution viscosity. The fabricated electrospun fibers of Au and Ag-loaded polymers show significant antibacterial activity against E. coli. Because of the wellknown antibacterial activity of Ag nanoparticles, these composite fibers can be used in fields, which need antibacterial properties by using environmentally friendly materials.



Figure 1. Synthesis of graft copolymers.

2. Results and Discussion

Vegetable oils (castor, limonene, and soybean) grafted metal (Ag, Pt, and Au) nanoparticles incorporated composite polymers were synthesized. The functional graft copolymers synthesis pathway was schematically depicted in **Figure 1**. The mixture of vegetable oil and metal precursor in an open glass container is exposed to air oxygen at room temperature to obtain oxidized vegetable oil polymer with metal NPs. During the autoxidation, radicals formed by the effect of daylight and air oxygen reduce the metal cations to metal atoms forming metal nanoparticles. The autoxidized vegetable oil polymers as macroperoxide initiator are used in the free radical polymerization of vinyl monomers.

The morphology of the prepared graft copolymers was evaluated based on their nanoparticle types. **Figure 2** shows the representative SEM micrographs of the cast films, which were prepared from Ag-loaded (left panel), Pt-loaded (right panel), and Au-loaded (bottom panel) polymers. Various samples of the functional polymers in film and powder form exhibit distinct texture profiles.

While film samples show smooth surfaces (Figure 2a–c,f,g,k), powder samples are porous and do not have regular structures (Figure 2d,e,h–j). However, when we take a closer look at their surfaces (seen in inset micrographs), the texture of samples changes and may have different characteristics than their general view. The polymers are composed of three constituents, monomer–oil–metal, and the presence of these constituents might be effective on the texture of samples. Elemental mapping by energy-dispersive X-ray spectroscopy (EDX) indicates metal NPs in the investigated regions (see Table S1, Supporting Information). The increment in Ag amount in polymers makes the Ag particles more visible and the shape of the particles changes from spherical to rod-like. The diameter of the NPs are in size \approx 50 nm (Figure 2a-c). On the other hand, Ag-loaded and ricinoleic acidbased PMMA and PS polymers have a larger Ag amount, the texture consists of agglomerations (Figure 2d,e). Pt-based polymers showed three distinctive textures. i) dispersed Pt NPs throughout the smooth polymeric surface (Figure 2f,g), ii) chain-like arrangement of the NPs, and iii) porous structure because of polystyrene matrix. Pt NPs are observed in sizes ranging from 50 to 80 nm in diameter. Figure 2k shows the Au-loaded polymer, which is synthesized via soybean oil and MMA monomer. The general overview of the polymer film is smooth but the closer view indicates the presence of Au NPs (around 75 nm) dispersed through the sample. Another observation is that limonene or soybean oilbased polymers have smoother surfaces than the ones synthesized via ricinoleic acid presumably due to its higher viscosity and triglyceride composition.[48]

Figure 3 shows the result of FTIR spectra of metal-loaded graft polymers which are mostly composed of methacrylate monomers. The spectra show characteristic signals at around 2995 and 2950 cm⁻¹ indicative for the vibrational modes of methacrylate and CH₃ asymmetric stretching vibrations of the ester-methylene group.^[49] The bands at 1725, 1146, and 1064 cm⁻¹ are assigned to C=O, C–O–C, and C–O stretching vibrations, respectively. The out-of-plane O–H bending vibrations occur at around 1435 cm⁻¹.^[50,51]

Most of the metal-loaded polymer consists of ricinoleic acid which is the primary constituent of castor oil. Ricinoleic acid has an uncommon molecular structure indicated to the hydroxyl group placed in the center of the unsaturated chain. Therefore, the hydroxyl group separated from the double bond by a

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Ag-loaded polymers Pt-loaded polymers (a) (f) 1 um 40 µm 40 µm (b) (g) 40 µm 40 µm (c) (h) 1 um 40 µm 4 um 40 µm 4 µm (e) 40...

Au-loaded polymer



Figure 2. SEM micrographs of the graft copolymers in film and powder forms a) AgPrici-MA-1, b) AgPrici-MA-3, c) AgPrici-MA-4, d) AgPMMArici-7, e) AgPSrici-8, f) PtLim-MA-3, g) PtPrici-MMA-3, h) PLimPt-MMA-2, i) PriciPt-MMA-2, j) PtPSLimox-6, and k) AuPsb-MMA-2. Insets show the closer magnification of the corresponding polymers.

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methylene group of ricinoleic acid intersect with the methacrylate bands.^[52] In addition, the presence of the most prominent carbonyl stretching band indicates autoxidation of vegetable oils employed in this study.^[53] For styrene-based copolymers, aromatic C–H and C=C stretching of the phenyl ring in polystyrene was observed at 3000-3100 and 1601 cm⁻¹, respectively.^[27,54]

UV-vis absorption spectra measured on dissolved Ag, Pt, and Au-loaded graft copolymers in N,N-dimethylformamide (DMF) are given in Figure 4. Polymeric ricinoleic acid containing Ag NPs exhibit maximum absorption at 433 nm, mainly confirming the formation of Ag NPs.^[54] A blue shift through different polymer matrices (MA, PMMA, and PS) is observed. Moreover, the broadening of absorption bands, particularly in the PMMA and PS composites (AgPMMArici-7 and AgPSrici-8) might be due to the agglomeration of Ag NPs which is consistent with the microscopy analysis. The absorption bands corresponding to the wavelength of around 285 nm belong to the Pt-loaded graft copolymers.^[55,56] Similarly, a broad absorption band is observed Pt-loaded for PS composite (Pt-PSLimox-6). Au-loaded graft copolymer reveals a sharp absorption band at 530 nm, which is characteristic of monodispersed spherical nanoparticles.^[57]

Figure 5 shows the TGA thermogram of three different metalloaded polymers. Because of the various constituents in polymer composites, each thermogram has different characteristics. Because the degradation temperature of PS occurs in single step, the polymers with PS moieties have single step degradation profiles, which are around 350 °C.^[58] On the other hand, the degradation of methylmethacrylate based polymers is more complex and during the thermal degradation, there are three main steps. The first step is around 150-250 °C range due to the decomposition of weak bonds followed by the decomposition of unsaturated chains around 250–300 °C and finally the third step comes after 300 °C, which is due to the random scisson of polymer chains.^[59-61] However, there are two steps in the methacrylate-based thermogram instead of three-step degradation profile. These unexpected variations in the degradation profile might be attributed to the presence of these vegetable oils. The thermal degradation of vegetable oils depends on their carbon to hydrogen ratios. It is known that the higher carbon/hydrogen (C/H) ratio is the higher the heat of combustion.^[62] Thus, different C/H ratios of ricinoleic acid, limonene, and soybean oil may result in the different thermal degradation profiles. For example, AgPrici-MA-1, AgPrici-MA-3, and AgPrici-MA-4 polymers have similar profiles but there are little differences due to the different ratios of constituents.

Electrospun fibers of graft copolymers are of great interest for their modification and applications. The functional graft copolymers with metal nanoparticles were processed by electrospinning to fabricate nanofibers. The morphology (shape and diameter) of the electrospun fibers depends not only on the properties of the polymer (type of polymer, the conformation of polymer chain or molecular weight, and glass-transition temperature) but also on the intrinsic solution parameters (electrical conductivity, surface tension, viscosity, viscoelasticity, and concentration).^[4,30,63] Moreover, the temperature and humidity have significant effects as well as system parameters such as collector type, tip-to-collector distance, potential difference, and feed rate of the solution. Table 1 summarizes the processing parameters of graft copolymers for the electrospinning and their fiber formation characteristics. Because the composition of each copoly-





Figure 3. FTIR spectra of a) AgPrici-MA-1, b) AgPrici-MA-3, c) AgPrici-MA-4, d) AgPMMArici-7, e) AgPSrici-8, f) PtLim-MA-3, g) PtPrici-MMA-3, h) PLimPt-MMA-2, i) PriciPt-MMA-2, j) PtPSLimox-6, and k) AuPsb-MMA-2 polymers.

mer is different from each other, although some of them seem identical, the electrospinning process was carried out by using different polymer solution concentrations, applied voltage, and feed rate. For the polymers with very low solution viscosity (i.e., Pt-PS-Limox-6, Ag-PS-rici-8, and Pt-Lim-MA-3), the polymer solution concentration was kept as 15.0 wt%, whilst it is 7.50 and 10.0 wt% for more viscous ones. Despite all efforts and different trials, PLim-Pt-MMA-2, and Prici-Pt-MMA-2 polymers were recorded as unspinnable due to their extremely low viscosity, electrospraying takes place instead.^[64]

The viscosity is determined by both concentration and the molecular weight of the polymers. When the polymer becomes longer, there will be a more intermolecular attraction between the chains, and the possibility of chain entanglement also increases.^[65] On the other hand, surface tension is related to viscosity. It is well known that the stronger the intermolecular interactions, the greater the surface tension.^[66] Thus, molecular weight, viscosity, and surface tension are all interrelated during the electrospinning process. At high polymer solution concentra-

tion, the entanglement of the chains enhance the formation of stable jet with higher mass transfer of the electrospinning solution, whilst low polymer solution concentration yields thin fibers and sometimes with beads.^[4]

Representative SEM micrographs of the graft copolymer nanofibers are given in **Figure 6**. It is well known that the concentration of polymer solution is one of the main parameters that if the concentration goes down below the 10 wt%, the potential difference atomizes the solution, and electrospraying starts.^[64] However, the effect of the presence of additives, such as oil and metals, cannot be ignored. In general, styrene-based graft copolymers have better fiber formation capability than the methacrylate-based ones. Figure 6d,g show the continuous and homogeneous distribution of fibers, which are styrene-based. On the other hand, it was hard to process the Pt-based graft-copolymers due to their low viscosity (Figure 6e,f). Especially the PtLim-MA-3 have lots of beads on the fibers and it was impossible to peel the collected fibers from aluminum foil. The Ag-loaded fibers with MMA and ricinoleic acid components have nearly

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Figure 4. UV-vis spectra of the polymer-vegetable oil graft copolymer containing metal NPs.

same spinnability and the resulting fibers have sub-micron diameters (Figure 6a–c). Whilst average fiber diameter (AFD) of Agbased polymers vary from 0.5 to 1.5 μ m, Pt-based polymers have AFD between 70 nm and 1.4 μ m diameter. Figure 6h shows the SEM micrograph of Au-Psb-MMA-2 graft copolymer, which results in the formation of continuous fibers with 1.0 μ m diameter.

The antibacterial activity of graft copolymers was studied by using Gram negative bacteria (*E. coli*). Some metal nanoparticles, such as Ag and Au, show antibacterial activity. Note that Ag is a very well-known antibacterial agent due to the positively charged ions. **Figure 7** shows the logarithmic growth of *E. coli* bacteria in the presence of Au or Ag-loaded graft copolymer fibers. The appearance of electrospun metal-loaded and control copolymer fibers before the antibacterial test (Figure 7a) and the bacteria cultures after treating with the electrospun copolymer fibers (Figure 7b) are demonstrated. The effect of Ag on the bacteria can be explained by several mechanisms that Ag⁺ ions bind to the cell

walls of bacteria and blocks the transport of nutrients through the cell. Moreover, Ag⁺ ions interacts with DNA and prevents the replication of cells or they may block the respiratory system by destroying the energy production.^[67,68] While Au-loaded polymer AuPsb-MMA-2 cuts the bacteria amount in the culture in half, the control sample, which does not contain Au nanoparticle and comprises of soybean oil and MMA constituents, also reduced the bacteria amount visibly. However, Ag-loaded graft copolymers have a significant antibacterial effect that no growth was observed in the presence of Ag-PMMA-rici-7 and Ag-PS-rici-8 fibers. When the control samples of these two polymers are considered, they inhibited the bacteria growth as in the control sample of Psb-MMA-2 fibers (nearly reduces the bacteria amount 50%) but Agloaded ones inhibit the bacteria growth 100% due to the antibacterial effect of Ag nanoparticles. The comparison of antibacterial activity was also compared with powder samples. Although Auloaded graft polymer powder shows relatively low antibacterial www.advancedsciencenews.com

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Figure 5. TGA thermogram of the polymer-vegetable oil graft copolymer containing metal NPs.

Table 1. Processing parameters of electros	pun fibers at 26.5 °C and 40% humidity.
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		Polymer solution [wt%]	Voltage [kV]	Feed rate [mL h ⁻¹]	Distance [cm]	Fiber Formation
Powder	Pt-PS-Limox-6	15.0	11	1.5	20.0	Uniform beadless
	Plim-Pt-MMA-2	7.50				Unspinnable
	Ag-PMMA-rici-7	7.50	15	2.0	20.0	Uniform beadless
	Prici-Pt-MMA-2	7.50				Unspinnable
	Ag-PS-rici-8	15.0	14	1.5	20.0	Uniform beadless
Film	Au-Psb_MMA-2	7.50	13	1.5	20.0	Uniform beadless
	Pt-Rici-MMA-3	10.0	20	1.5	20.0	Beaded
	Pt-Lim-MA-3	15.0	15	2.0	20.0	Beaded
	Ag-Prici-MA-4	10.0	20	2.5	20.0	Beaded
	Ag-Prici-MA-3	10.0	12	2.0	20.0	Beaded
	Ag-Prici-MA-1	7.50	-	-	-	Unspinnable

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Figure 6. SEM micrographs of the electrospun fibers a) AgPrici-MA-3, b) AgPrici-MA-4, c) AgPMMArici-7, d) AgPSrici-8, e) PtLim-MA-3, f) PtPrici-MMA-3, g) PtPSLimox-6, and h) AuPsb-MMA-2. Insets show the closer magnification of corresponding polymers and histogram of fiber diameter distribution.

activity than the corresponding fibers, Ag-loaded powder shows similar activity as its corresponding control sample. Thus, the advantage of electrospun fibers with mechanical integrity compared to the powder samples in terms of their being free-standing was represented.

Currently, the most promising direction for ongoing and future work appears to find novel material preparation method in green approach. One point to take into account is the limited primary sources of petroleum products and their hazardous effect on the environment. To this end, the choice of monomers and initiators has been gaining significant attention in the environmentally friendly polymer synthesis processes. The use of vegetable oil-based macroperoxide initiators not only reduces the consumption of initiators but also provides bio-based com-



Figure 7. Photographic images of a) electrospun metal-loaded and control copolymer fibers and b) bacteria cultures after the antimicrobial test. c) Bacterial growth of *E. coli* against different amounts of the metal loaded powder and fiber graft copolymers. The dotted lines show the logarithmic bacterial concentration in the control samples.

posite materials. Another important point is the inert behavior of metal nanoparticles employed in this study that do not contribute/prevent free radical bulk polymerization. It is noteworthy to mention that if the nanoparticle amount was kept only around the critical value, the formation of an undesirable network structure is inhibited suppressing the gel effect in the polymerization.^[69] The advantageous combination of bio-based functional copolymers and high-surface-area nanofibers provides ease of handling as well as support materials for a wide variety of green applications.

3. Conclusions

Vegetable oils are of great importance in synthesizing biomaterials as they are both available from renewable resources and tend to react with molecular oxygen. This work proves the use of autoxidized vegetable oils as macroperoxide nanocomposite initiators containing metal nanoparticles in free radical polymerization of vinyl monomers. When the environmental damage of using initiators was considered, the utilization of autoxidized vegetable oils as macroperoxide nanocomposite initiators offers a

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significant minimization in initiator consumption in the polymer synthesis schemes. The composite methacrylate and styrenebased graft copolymers with autoxidized vegetable oils (castor, limonene, and soybean) and metal nanoparticles (Ag, Pt, and Au) were successfully synthesized and processed by electrospinning. Because of the different physical characteristics of polymer solutions, that is, solution viscosity, not all polymers can be electrospun successfully but Ag-based graft-copolymers were processed better than Pt-based ones. The Ag, Pt and Au-based polymers provide insoluble polymeric support for antibacterial activity applications. Especially Ag-based graft copolymer fibers show significant antibacterial activity against E. coli. Thus, these organic-inorganic hybrid copolymers can be potentially applied as support material for antibacterial surfaces and they are suitable for various applications such as wound dressing, tissue engineering, catalytic and sensing applications.

4. Experimental Section

Materials: Castor oil was supplied by a local stock market in Turkey (originally from India, purity: 86–90 wt%). Limonene was gift from Acar Kimya, İstanbul, Turkey, purity: 98%). Soybean oil was a gift from CHS (Istanbul, Turkey). It contains palmitic acid (11.6 wt%), stearic acid (4.9 wt%), oleic acid (33.7 wt%), linoleic acid (42.0 wt%), and linolenic acid (3.63 wt%). HAuCl₄, AgNO₃, H₂PtCl₆ were supplied from Sigma-Aldrich, Germany. Methyl methacrylate and styrene were supplied from Sigma-Aldrich, Germany. They were passed through an Al₂O₃ column before use.

Synthesis of Polymers: For the synthesis of ricinoleic acid from castor oil, a mixture of ethyl alcohol (500 mL) and KOH (85.6 g) was stirred until clear solution was obtained. Castor oil (318 g) was added to this solution at 67 °C and continued stirring for 190 min. After cooling the solution at room temperature, the solution was acidified by carefully adding 60 mL 1 m

 Table 2. The reagents used in production of macroperoxide initiators.

 H_2SO_4 . The ricinoleic acid layer at the top was separated and washed with distilled water (500 mL) in two times. It was dried on anhydrous Na_2SO_4 . The obtained product was 260 g. A mixture of ricinoleic acid with or without H_2PtCl_6 , $AgNO_3$, or $HAuCl_4$ was spread out into a Petri dish ($\Theta = 20$ cm, oil thickness: 1.1 mm) where it was exposed to daylight and white light (18 W) in the air at room temperature. After a given time, a pale yellow viscous liquid, autoxidation product, ricinoleic acid polymeric peroxide (Prici), was formed. The reagents used in production of the Prici-peroxide samples were listed in **Table 2**. For the synthesis of autoxidized limonene, oxygen gas was introduced into the liquid limonene (17.2 g in a glass bottle) for 5 min exposing white light (15 W lamp) at room temperature for 6 days.

Free radical polymerization (with or without toluene) of methyl methacrylate (or styrene) was initiated by the autoxidized macroperoxide initiator. The mixture of as-synthesized initiator was dissolved in 5 mL of toluene in a reaction bottle. Argon was introduced into the tube for about 1 min to expel the air. After polymerization reaction was completed, the polymer was precipitated into methanol (200 mL) under vigorous stirring. The polymer obtained was filtered from methanol and dried under vacuum at 40 °C for 24 h. The details were given in **Table 3**.

Fabrication of Electrospun Nanofibers: The obtained polymer powder and film composites were dissolved in DMF to investigate their electrospinning characteristics. The weight ratio of polymer solution was arranged as 7.5% and 15% which were given in Table 1.

The viscosity of selected polymer solutions was determined using a rotational viscometer (Thermo Scientific HAAKE Viscotester C, Massachusetts, USA) with a L2 spindle, where the rotational velocity of the spindle was 200 rpm at 23 °C. The polymer solution concentration was kept as 1.5 wt%. The viscosity values of Ag-PMMA-rici-7, Ag-Prici-MA-4, Pt-Lim-MA-3 were measured as 8.2, 5.8, and 4.9 mPa s, respectively. The prepared polymer solutions were supplied into a 10 mL syringe. The electrospinning process was performed at the temperature and humidity on average 26.5 °C and 40%, respectively, and the solutions were injected from the syringe pump (New Era Pump Systems, Inc. NE-300) with a feed rate of between 1.5 and 2.5 mL h⁻¹. Using a high-voltage power supply at

Initiator name	Ricinoleic acid [g]	Soybean oil [g]	AgNO ₃ [g]	H ₂ PtCl ₆ [g]	HAuCl ₄ [g]	Time [day]
PtRici-3m	78.4	-	-	1.71	-	90
AgPrici-78	78.4		4.51			90
AgPrici-37	37.9		3.79			90
AgPrici-75d-1	31.3		3.01			30
Prici-ox	72.1					75
Psb20Au1.6		20.0			1.20	29

Table 3. Free radical polymerization of vinyl polymers with the macroperoxide initiators 80 °C.

Sample name	Initator type	Initator amount [g]	MMA [g]	Styrene [g]	Toluene [g]	Time [min]	Yield [g]
Ag-Prici-MA-1	AgPrici3m	1.04	5.06	-	3.0	90	1.43
Ag-Prici-MA-3	AgPrici3m	1.04	8.16	-	3.0	90	2.60
Ag-Prici-MA-4	AgPrici-75d-1	7.61	12.6	-	-	90	6.24
Ag-PMMA-rici-7	AgPrici-75d-1	1.02	10.1	-	-	180	2.47
Prici-Pt-MMA-2	Pt-Prici-3m	1.11	5.06	-	3.0	-	0.43
Pt-Rici-MMA-3	Pt-rici-04	5.15	10.2	-	-	90	2.91
Plim-Pt-MMA-2	Plimox-Pt-1	1.04	3.02	-	5.0	90	0.82
Pt-Lim-MA-3	Plimox-Pt-1	3.74	8.11	-	-	450	3.57
Au-Psb-MMA-2	AuPsb29d.1.frks	3.88	10.5	-	3.61	360	1.15
Pt-PS-Limox-6	PLmnoxPt-1	1.03	-	10.1	-	300	2.36
Ag-PS-rici-8	AgPrici78	1.06		10.1	-	300	2.26

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a range of 11 to 15 kV, a jet ejected the polymer solution through the needle tip. The electrospun nanofibers were assembled on a stable collector which was aluminum foil placed at a 20 cm distance.

Characterization of Polymers and Nanofibers: The morphology and texture of the nanofibers were characterized by a SEM (Carl Zeiss 300VP, Germany) equipped with an EDX system. The samples were coated with gold to enhance the conductivity by using Q150 RES before SEM imaging. The applied voltage and working distance of the SEM imaging were 5 kV and between 5.4–7.1 mm, respectively. FTIR and the attenuated total reflection of the samples were studied in the range of 4000–450 cm⁻¹ in the transmission mode by using a Perkin Elmer spectrum two. UV–vis absorption spectra of all polymers in DMF were recorded on a Hach DR6000 UV– vis laboratory spectrophotometer in the range of 250–800 nm. TGA was performed by Perkin Elmer Diamond TG/DTA at a temperature of 25 up to $650 \,^\circ$ C at a heating rate of 10 $^\circ$ C min⁻¹ and under the nitrogen atmosphere at 50 mL min⁻¹ flow rate.

Antimicrobial Activity Analysis: Gram-negative E. coli (ATCC 25922) bacteria were used to investigate the antimicrobial activity of metal-loaded polymers. The bacteria culture was cultivated overnight in nutrient broth (NB) through a conventional antimicrobial activity assay. Then, they were transferred into a test tube and their optical density was adjusted to the 0.5 McFarland standard by adding peptone water (DEN-1Densitometer, Riga, Latvia). The bacteria culture was diluted to 10⁵ CFU mL⁻¹ concentrations with NB. After overnight incubation microbial concentration was set to 10^{6} mL⁻¹. To evaluate the antimicrobial activity, the same amount of metal-loaded polymers and the bacteria culture were added into the buffer solution. Also, the control samples were prepared for E. coli without adding any metal-loaded polymers. Three experiments were performed for each sample and bacterial culture, and the bacterial culture was cultured for 24 h in an incubation shaker at 37 °C and 200 rpm. Each cultured bacterial culture was diluted in peptone water at a 1:10 ratio. This procedure was carried out until the sixth dilution. After that, 100 mL of each sample (stock and diluted) was transferred onto NB agar plates. The plates were incubated at 37 °C for 24 h and inspected for growth. The number of viable bacteria was then counted and converted to CFU mL⁻¹. This antimicrobial activity analysis was performed by modifying ASTM e2149.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

autoxidation, metal nanoparticles, methacrylate, polystyrene, vegetable oils

- [1] C. Zhang, T. F. Garrison, S. A. Madbouly, M. R. Kessler, *Prog. Polym. Sci.* 2017, *71*, 91.
- [2] C. K. Williams, M. A. Hillmyer, Polym. Rev. 2008, 48, 1.
- [3] T. Isık, M. M. Demir, Fibers Polym. 2018, 19, 767.
- [4] T. Isık, M. M. Demir, Sustainable Mater. Technol. 2018, 18, e00084.
- [5] P. T. Anastas, J. C. Warner, *Frontiers* **1998**, *640*, 1998.
- [6] A. Sionkowska, Prog. Polym. Sci. 2011, 36, 1254.
- [7] L. Fertier, H. Koleilat, M. Stemmelen, O. Giani, C. Joly-Duhamel, V. Lapinte, J.-J. Robin, Prog. Polym. Sci. 2013, 38, 932.
- [8] D. P. Pfister, Y. Xia, R. C. Larock, ChemSusChem 2011, 4, 703.
- [9] T. F. Garrison, A. Murawski, R. L. Quirino, Polymers 2016, 8, 262.
- [10] J. Salimon, B. M. Abdullah, R. M. Yusop, N. Salih, *Chem. Cent. J.* 2014, 8, 1.
- [11] M. Soucek, T. Khattab, J. Wu, Prog. Org. Coat. 2012, 73, 435.
- [12] A. Can, H. Sivrikaya, B. Hazer, Int. Biodeterior. Biodegrad. 2018, 133, 210.
- [13] A. Allı, S. Allı, C. R. Becer, B. Hazer, Eur. J. Lipid Sci. Technol. 2016, 118, 279.
- [14] B. Hazer, E. Ayyıldız, F. Bahadır, J. Am. Oil Chem. Soc. 2017, 94, 1141.
- [15] B. Çakmaklı, B. Hazer, İ. Ö. Tekin, Ş. Açıkgöz, M. Can, J. Am. Oil Chem. Soc. 2007, 84, 73.
- [16] Ö. Ince, E. Akyol, E. Sulu, T. Şanal, B. Hazer, J. Polym. Res. 2016, 23, 5.
- [17] G. Totaro, L. Cruciani, M. Vannini, G. Mazzola, D. Di Gioia, A. Celli, L. Sisti, *Eur. Polym. J.* 2014, 56, 174.
- [18] H. Koc, E. Kilicay, Z. Karahaliloglu, B. Hazer, E. B. Denkbas, J. Biomater. Appl. 2021, 36, 385.
- [19] J. Ghitman, R. Stan, S. Cecoltan, M. C. Chifiriuc, H. Iovu, J. Drug Delivery Sci. Technol. 2018, 46, 162.
- [20] G. Gallon, V. Lapinte, J.-J. Robin, J. Chopineau, J.-M. Devoisselle, A. Aubert-Pouessel, ACS Sustainable Chem. Eng. 2017, 5, 4311.
- [21] T. Lu, Y. Deng, J. Cui, W. Cao, Q. Qu, R. Xiong, W. Ma, J. Lei, C. Huang, ACS Appl. Mater. Interfaces 2021, 13, 22874.
- [22] M. Zhua, D. Hua, H. Pan, F. Wang, B. Manshian, S. J. Soenen, R. Xiong, C. Huang, J. Colloid Sci. 2018, 511, 411.
- [23] D. Lv, R. Wan, G. Tang, Z. Mou, J. Lei, J. Han, S. D. Smedt, R. Xiong, C. Huang, ACS Appl. Mater. Interfaces 2019, 11, 12880.
- [24] W. R. Rolim, M. T. Pelegrino, B. de Araújo Lima, L. S. Ferraz, F. N. Costa, J. S. Bernardes, T. Rodigues, M. Brocchi, A. B. Seabra, *Appl. Surf. Sci.* 2019, 463, 66.
- [25] V. Gopinath, S. Priyadarshini, M. F. Loke, J. Arunkumar, E. Marsili, D. MubarakAli, P. Velusamy, J. Vadivelu, *Arabian J. Chem.* 2017, 10, 1107.
- [26] A. Kumar, P. K. Vemula, P. M. Ajayan, G. John, Nat. Mater. 2008, 7, 236.
- [27] B. Hazer, Ö. A. Kalaycı, Mater. Sci. Eng., C 2017, 74, 259.
- [28] B. Cakmaklı, B. Hazer, Ş. Açıkgöz, M. Can, F. B. Cömert, J. Appl. Polym. Sci. 2007, 105, 3448.
- [29] T. Isik, N. Horzum, Ü. H. Yıldız, B. Liedberg, M. M. Demir, Macromol. Mater. Eng. 2016, 301, 827.
- [30] A. Greiner, J. H. Wendorff, Angew. Chem., Int. Ed. 2007, 46, 5670.
- [31] M. H. Elhousseini, T. Isık, Ö. Kap, F. Verpoort, N. Horzum, Appl. Surf. Sci. 2020, 514, 145939.
- [32] T. J. Sill, H. A. Von Recum, *Biomaterials* 2008, 29, 1989.
- [33] H. M. Powell, D. M. Supp, S. T. Boyce, *Biomaterials* 2008, 29, 834.
- [34] D. Liang, B. S. Hsiao, B. Chu, Adv. Drug Delivery Rev. 2007, 59, 1392.
- [35] X. Hu, S. Liu, G. Zhou, Y. Huang, Z. Xie, X. Jing, J. Controlled Release 2014, 185, 12.

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- [36] I. Han, K. J. Shim, J. Y. Kim, S. U. Im, Y. K. Sung, M. Kim, I.-K. Kang, J. C. Kim, Artif. Organs 2007, 31, 801.
- [37] J. Zeng, X. Xu, X. Chen, Q. Liang, X. Bian, L. Yang, X. Jing, J. Controlled Release 2003, 92, 227.
- [38] T. A. Arica, T. Isık, T. Guner, N. Horzum, M. M. Demir, Macromol. Mater. Eng. 2021, 2100143.
- [39] C. Gualandi, A. Celli, A. Zucchelli, M. L. Focarete, Organ.-Inorgan. Hybrid Nanomater. 2014, 87.
- [40] Q. Saiding, W. Cui, Nano Sel. 2021.
- [41] E. Berber, N. Horzum, B. Hazer, M. M. Demir, *Fibers Polym.* 2016, 17, 760.
- [42] R. Sridhar, R. Lakshminarayanan, K. Madhaiyan, V. A. Barathi, K. H. C. Lim, S. Ramakrishna, *Chem. Soc. Rev.* 2015, 44, 790.
- [43] N. Horzum, M. M. Demir, M. Nairat, T. Shahwan, RSC Adv. 2013, 3, 7828.
- [44] N. Horzum, D. Tascioglu, C. Özbek, S. Okur, M. M. Demir, New J. Chem. 2014, 38, 5761.
- [45] Z. Zhang, Y. Wu, Z. Wang, X. Zou, Y. Zhao, L. Sun, Mater. Sci. Eng., C 2016, 69, 462.
- [46] S. Poyraz, I. Cerkez, T. S. Huang, Z. Liu, L. Kang, J. Luo, X. Zhang, ACS Appl. Mater. Interfaces 2014, 6, 20025.
- [47] S.-S. Kim, H. Ha, C. J. Ellison, ACS Sustainable Chem. Eng. 2018, 6, 8364.
- [48] T. M. Serra, D. R. De Mendonca, J. P. Da Silva, M. R. Meneghetti, S. M. P. Meneghetti, *Fuel* **2011**, *90*, 2203.
- [49] S. B. Aziz, O. G. Abdullah, A. M. Hussein, H. M. Ahmed, Polymers 2017, 9, 626.
- [50] D. Sugumaran, K. Karim, eProc. Chem. 2017, 2, 1.
- [51] S. Sathish, B. C. Shekar, Indian J. Pure Appl. Phys. 2014, 52, 64.
- [52] T. A. McKeon, Ind. Oil Crops 2016, 2016, 275.

- [53] E. Ilhan, Z. Karahaliloglu, E. Kilicay, B. Hazer, E. B. Denkbas, Mater. Technol. 2020, 35, 179.
- [54] A. Can, S. Palanti, H. Sivrikaya, B. Hazer, F. Stefani, Cellulose 2019, 26, 5075.
- [55] T. D. Nguyen, Q. D. Nguyen, T. T. Nguyen, T. B. Nguyen, Adv. Nat. Sci. Nanosci. Nanotechnol. 2014, 5, 035011.
- [56] L. Guo, L. Mao, K. Huang, H. Liu, J. Mater. Sci. 2017, 52, 10738.
- [57] M. Zimbone, L. Calcagno, G. Messina, P. Baeri, G. Compagnini, *Mater. Lett.* 2011, 65, 2906.
- [58] S. Seleem, M. Hopkins, J. Olivio, D. Schiraldi, Ohio J. Sci. 2017, 117, 50.
- [59] S. R. Valandro, P. C. Lombardo, A. L. Poli, M. A. Horn, M. G. Neumann, C. C. S. Cavalheiro, *Mater. Res.* 2014, 17, 265.
- [60] M. M. Demir, P. Castignolles, Ü. Akbey, G. Wegner, Macromolecules 2007, 40, 4190.
- [61] S. Hess, M. M. Demir, V. Yakutkin, S. Baluschev, G. Wegner, Macromol. Rapid Commun. 2009, 30, 394.
- [62] J. M. Smith, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, New York, NY 1950.
- [63] M. M. Demir, I. Yilgor, E. Yilgor, B. Erman, Polymer 2002, 43, 3303.
- [64] T. Isık, M. M. Demir, C. Aydogan, M. Ciftci, Y. Yagci, J. Polym. Sci., Part A: Polym. Chem. 2017, 55, 1338.
- [65] J. Zheng, A. He, J. Li, J. Xu, C. C. Han, Polymer 2006, 47, 7095.
- [66] H. Schonhorn, J. Chem. Eng. Data 1967, 12, 524.
- [67] A. B. Lansdown, J. Wound Care 2002, 11, 125.
- [68] K. Nielsen Silver. A powerful weapon against microbes. https: //www.coloplast.com/products/wound/articles/silver-a-powerfulweapon-against-microbes/#section=Reference-list_463946 (accessed: November 2021).
- [69] M. M. Demir, G. Wegner, Macromol. Mater. Eng. 2012, 297, 838.

